

Analysis of p - n Luminescence in Zn-Doped GaP

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p - n luminescence and photoluminescence of Zn-doped GaP are investigated. Spectral distributions and the light output as a function of temperature and excitation density are recorded. The light output of the p - n luminescence shows a strongly superlinear dependence on excitation density. With rising temperature, the superlinear range shifts to higher excitation densities. Using a three-level model the recombination kinetics are analyzed with the aid of the Klasens code-number method. The analysis given allows an interpretation of the superlinearity and gives a quantitative explanation of the observed shift of the superlinear range with temperature.

1. INTRODUCTION

TO produce efficient p - n light sources, a substance is needed which is a good phosphor and at the same time a semiconductor which can be made low-ohmic n type and p type.

Efficient phosphors of the ZnS type contain radiative recombination centers which are represented in the energy diagram by rather deep levels, and which act as effective traps for either holes or electrons. The rather low thermal release of these holes or electrons from the traps prevents nonradiative recombinations via quenching levels, which in actual phosphors are always present.

Good conductivity on the other hand calls for shallow levels. However these shallow levels have bad trapping properties and therefore radiative recombinations via these levels are not likely to occur.

In order to produce the luminescence with good efficiency, and at the same time obtain good conductivity, both shallow and deep levels should be introduced, that is to say deep hole traps (acceptors) in the n region and deep electron traps (donors) in the p region.

We have tried to find suitable materials among the III-V compounds because they can be made n and p type and because several members of this group show good fluorescence properties. GaN for instance can be activated and coactivated with a large variety of elements, and then shows photoluminescence, C. R. luminescence, and (weak) electroluminescence.^{1,2} The luminescence behavior in GaN proved to be very similar to that of ZnS or CdS. For instance, we were able to measure photoconductivity, glow curves, and infrared quenching of luminescence. A further investigation of the potentialities of GaN for p - n light sources however, failed because of technological difficulties in preparing large crystals of GaN.

In this respect GaP³ and AlP⁴ are more favorable. Polycrystalline samples of these substances were found to show both p - n luminescence and photoluminescence. However, the efficiency was low because only shallow levels were present. We therefore tried to prepare GaP with both shallow and deep levels. Incorporation of Zn appeared to be fruitful in this respect because it introduces deep levels at 0.4 eV from the valence band which show good radiative recombination properties. In fact p - n light sources prepared from Zn-doped GaP showed a hundred to a thousand fold increase in efficiency, as compared to p - n light sources from GaP which were not doped with Zn.

The present paper reports on the electrical and optical properties of these Zn-doped GaP samples. It will be shown that the p - n luminescence behavior in GaP-Zn corresponds so closely to the luminescence behavior in the classical ZnS phosphors, that the same methods of analysis can be applied.

2. EXPERIMENTS

The method of preparing the GaP crystals was similar to the one described in a previous paper,³ the only difference being a small addition of ZnO to the Ga prior to the reaction with P.

In the temperature range between 90° and 500°K,³ undoped GaP showed only one activation energy for both n -type and p -type conductivity. Near room temperature the conductivity was already saturated. The Zn-doped p -type crystals, however, contained deeper acceptor levels, as is evident from the fresh increase in conductivity at higher temperatures shown in Fig. 1, which can be correlated with an activation energy of 0.4 eV (see Sec. 3).

The electroluminescence in undoped GaP was shown³ to be due to a radiative recombination of charge carriers within, or in the neighborhood, of p - n junctions. In

¹ H. G. Grimmeiss and H. Koelmans, Z. Naturforsch. **14a**, 264 (1959).

² H. G. Grimmeiss, R. Groth, and J. Maak, Z. Naturforsch. **15a**, 799 (1960).

³ H. G. Grimmeiss and H. Koelmans, Philips Research Repts. **15**, 290 (1960).

⁴ H. G. Grimmeiss, W. Kischio, and A. Rabenau, J. Phys. Chem. Solids **16**, 302 (1960).

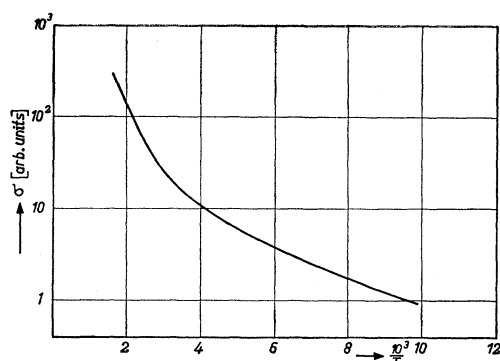


FIG. 1. Temperature dependence of the conductivity in GaP-Zn.

contrast to these first experiments where a point-contact electrode was used, the present work was performed with large-area electrodes of gallium or silver paint.

With alternating current the crystals only showed luminescence during one half-cycle (Fig. 2). The direction of the current during this half-cycle corresponded to the forward direction of the p - n junction. On the other hand, the photocurrent induced by irradiation of the p - n junction flowed in the reverse direction of the p - n junction.⁵

The p - n luminescence spectrum in undoped GaP consists of two bands, one at about 2.2 eV (5650 Å) and one at about 2.0 eV (6200 Å).³ Doping with Zn introduces a new broad band with a maximum at 1.77 eV (7000 Å) (Fig. 3). At the same time the 6200-Å band disappears. Figure 3 shows the spectral distributions at room temperature.

The spectral distributions were also measured at liquid-air temperature (Fig. 4). Comparison between Figs. 3 and 4 shows that the 5650-Å band does not shift on cooling.

At low temperatures both emission bands narrow and the low energy emission shows a slight shift from 1.77 eV to 1.82 eV (6800 Å). Figure 4 also indicates an increase of the relative intensity of the 5650-Å band at low temperatures.

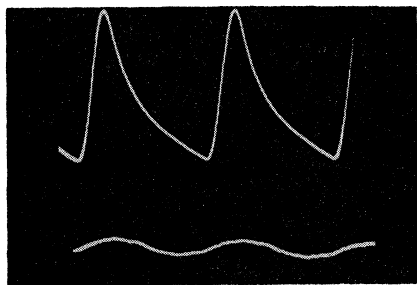


FIG. 2. p - n luminescence with excitation by alternating current. Upper curve: luminescence (current in CdS cell) versus time. Lower curve: voltage versus time (GaP-Zn).

⁵ H. G. Grimmeiss, W. Kischio, and H. Koelmans, J. Solid State Electr. (to be published).

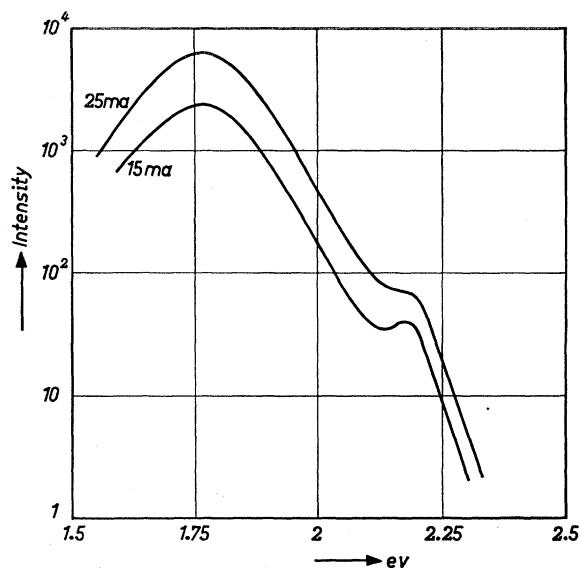


FIG. 3. Spectral distribution of the p - n luminescence in GaP-Zn at 20°C for two values of the current.

Klasens⁶ and Schön⁷ have shown that in ZnS-type phosphors, an analysis of the dependence of the luminescence on excitation-density can give valuable information about the recombination mechanism. Bearing in mind that in a p - n diode, biased in the forward direction the electric current is a measure of the injection and hence of the excitation-density, we measured the intensity of the p - n luminescence as a function of the current. Figure 5 gives a double logarithmic plot of these

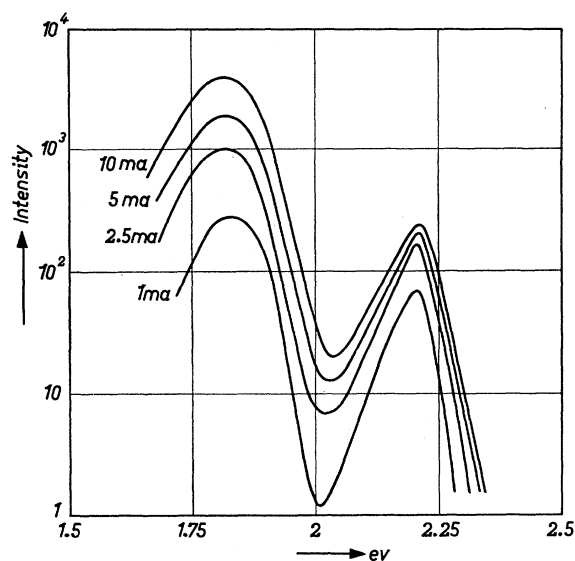


FIG. 4. Spectral distribution of the p - n luminescence in GaP-Zn at about -170°C for different values of the current.

⁶ H. A. Klasens, J. Phys. Chem. Solids **7**, 175 (1958).

⁷ M. Schön, *Halbleiterprobleme IV*, edited by W. Schottky (Frederick Vieweg and Sohn, Braunschweig, Germany, 1958), p. 283.

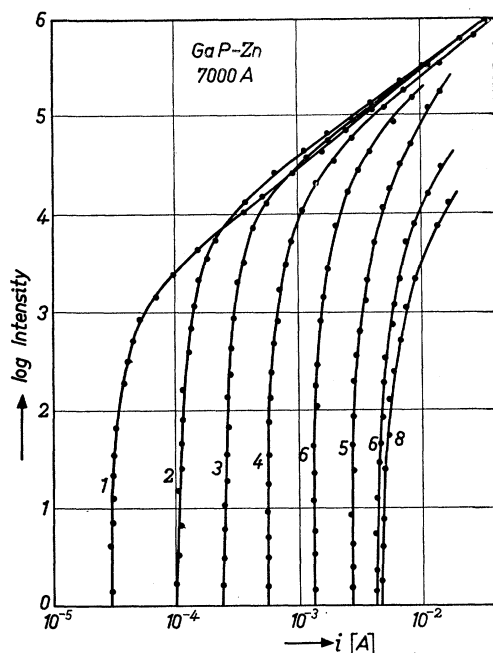


FIG. 5. The intensity of the red emission (7000 Å) in GaP-Zn as a function of the current at different temperatures. (1) -175°C ; (2) -160°C ; (3) -146°C ; (4) -130°C ; (5) -107°C ; (6) -70°C ; (7) -20°C ; (8) $+20^{\circ}\text{C}$.

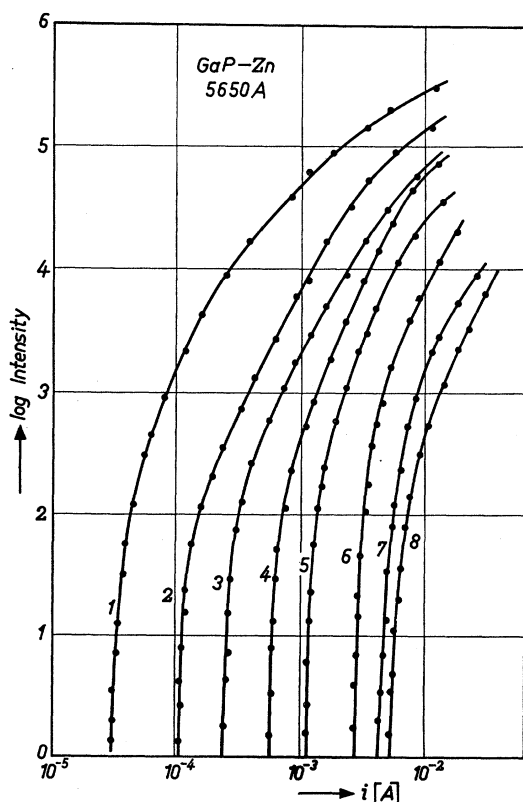


FIG. 6. The intensity of the green emission (5650 Å) in GaP-Zn as a function of the current at different temperatures (same temperatures as in Fig. 6).

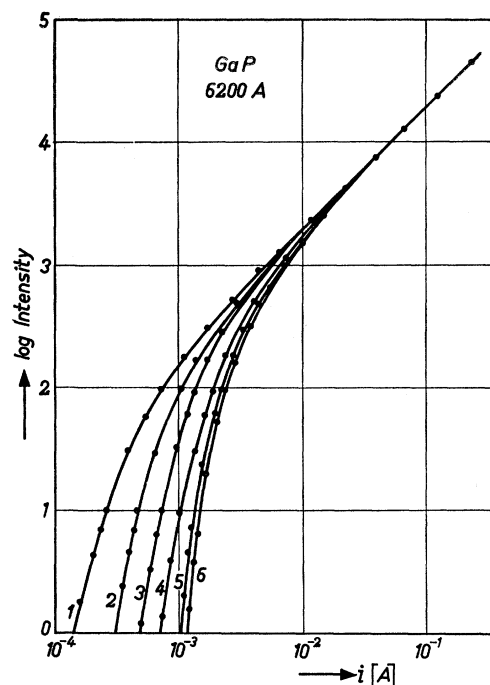


FIG. 7. The intensity of the yellow emission in undoped GaP (6200 Å) as a function of the current at different temperatures. (1) -172°C ; (2) -160°C ; (3) -148°C ; (4) -130°C ; (5) -70°C ; (6) $+20^{\circ}\text{C}$.

measurements for the 7000-Å emission in Zn-doped GaP at different temperatures. Each of the curves (Fig. 5) consists of two parts, a strongly superlinear part with a slope of about 20 at low currents, followed by a linear part at higher currents. The linear part does not depend essentially on temperature, whereas the superlinear part shifts to larger currents with increasing temperature.

A similar type of behavior has already been found and discussed for the photoconductivity⁸ and photoluminescence.⁹ As in CdS and CdSe for instance, the steep curves in Fig. 5 would probably bend to a lower slope at still smaller values of the excitation density, but the luminescence intensity was too small to measure a change of slope in this region.

The green emission band at 5650 Å was studied in the same way and was found to behave similarly (Fig. 6). For comparison, Fig. 7 shows the same type of curves for the 6200-Å band in undoped GaP. Here it is clear that at high currents all curves merge into the same line with slope 1.

Figure 8 gives the intensity I of the two p - n luminescence-bands (at constant, high current) as a function of temperature. The curves show the well-known behavior in fluorescence of ZnS-type phosphors. With decreasing temperature, the long-wave emission first in-

⁸ R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960).

⁹ N. R. Nail, F. Urbach, and D. Pearlman, *J. Opt. Soc. Am.* **39**, 690 (1949).

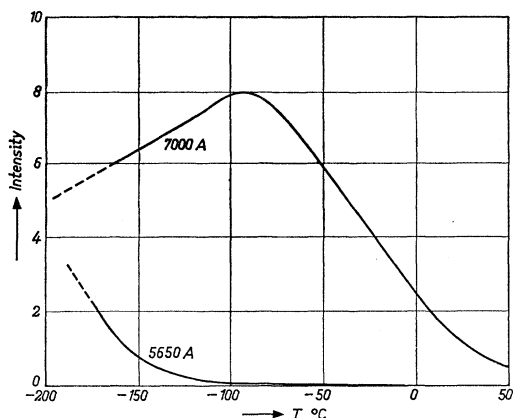


FIG. 8. Temperature dependence of the p - n luminescence in GaP-Zn.

creases and then passes through a maximum when the short-wave band begins to appear. In many crystals the temperature quenching of the 7000-Å band was already effective at much lower temperatures. In these crystals the position of the maximum, if present, was at such a low temperature that we could not measure it.

For investigating the photoluminescence, the Zn-doped GaP crystals were powdered. Because of temperature quenching, the spectral distribution could only be measured at liquid-air temperature (Fig. 9). In contrast to the curves measured for the p - n luminescence (cf. Fig. 4) the spectral distribution for the photoluminescence shows a band at about 2.03 eV (6100 Å) in addition to the main band at 1.82 eV.

The photoluminescence spectrum therefore agrees with that of undoped GaP, in as far as in this case only a band at approximately 2.0 eV was found and the 2.2

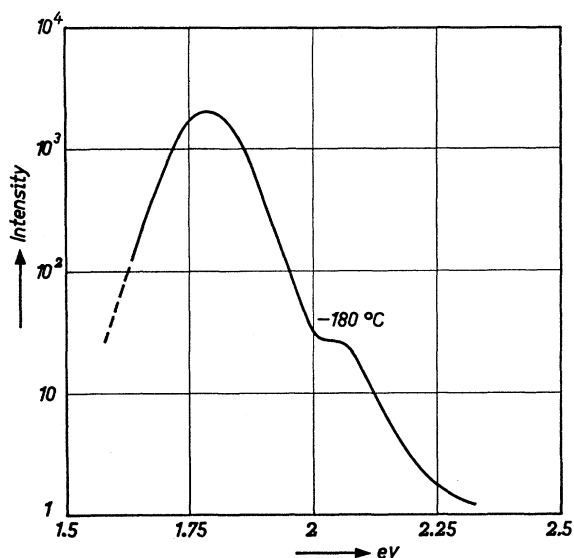


FIG. 9. Spectral distribution of the photoluminescence in GaP-Zn at liquid air temperature (excitation with 3650 Å).

ev band, present in the p - n luminescence spectrum, was also absent with photo-excitation.³

When measuring the temperature dependence of the photoluminescence (Fig. 10), we found that the temperature quenching was already active at such low temperatures, that a maximum of the luminescence could not be reached within the temperature range covered by the experiments. In view of the fact that the level produced by Zn-doping is at 0.4 eV from the valence band, one might perhaps expect temperature quenching at much higher temperatures. The early quenching of the p - n luminescence in the crystals seems to indicate a rather high concentration of killer centers. Moreover the excitation density in photoluminescence is much lower than in p - n luminescence. This circumstance will also contribute in lowering the quenching temperature in photoluminescence.

The intensity dependence of the photoluminescence was investigated at two temperatures, viz. -180° and

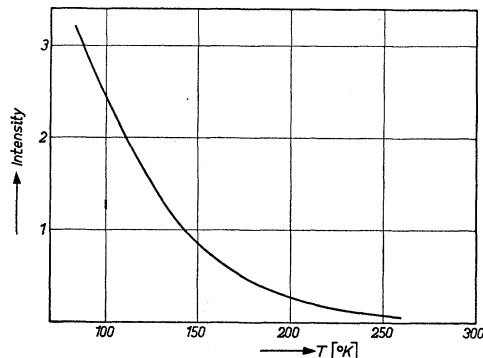


FIG. 10. Temperature dependence of the photoluminescence in GaP-Zn.

-150°C . The excitation density was varied by changing the distance from the sample to the exciting light source. At both temperatures the intensity of the photoluminescence changes linearly with excitation density over the whole range studied (Fig. 11).

3. DISCUSSION

In Sec. 2 it was shown that doping with Zn causes another increase in p -type conductivity at higher temperatures. The activation energy deduced from this conductivity rise was $E_a = 0.4$ eV. This value was obtained from the relationship $p \sim \exp[-E_a/2kT]$. The reason why the exponent contains $E_a/2$ instead of E_a comes from the fact that in the p region shallower acceptor levels are also present, which are wholly or partially occupied by holes at low temperature and which account for the initial rise of conductivity in the low-temperature region.

An independent determination of E_a is found from the equation $E_a \approx E_{\text{gap}} - E_{\text{max}}$,³ where E_{gap} is the band gap energy and E_{max} is the energy corresponding to the maximum of the p - n and photoluminescence in GaP-Zn

at 1.8 ev. This gives $E_a \approx 2.25 - 1.8 = 0.45$ ev which agrees reasonably well with the value 0.4 obtained from the analysis of electrical data. Together with the results obtained for undoped GaP, and in agreement with the results from the study of the extrinsic photovoltaic effect,⁵ the level scheme for GaP-Zn as shown in Fig. 12 was constructed. Apart from the level caused by Zn, one additional acceptor level and one donor level are present, which are probably due, respectively, to Ga and P vacancies.³ Furthermore, because even in the linear range at high currents the efficiency is rather low, we also have to assume radiationless recombinations, which may be caused by quenching levels as well as by radiationless band-band recombination. As yet nothing is known about the actual position of the quenching levels, but we shall suppose them to be deep donor levels. With the aid of the level scheme of Fig. 12, we tried to analyze

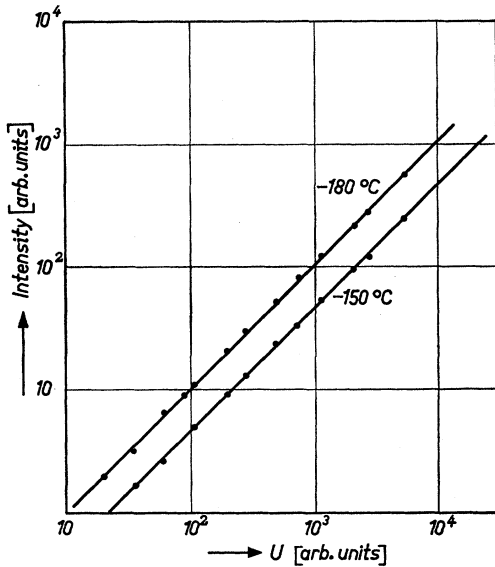


FIG. 11. The photoluminescence in GaP-Zn as a function of the excitation density at two different temperatures.

the kinetics of the recombination of electrons and holes in Zn-doped GaP.

Recently Klasens⁶ gave a systematic analysis of the kinetics of the transitions in (ZnS-type) phosphors and photoconductors. Using a model with two levels within the forbidden energy gap, he could indicate the conditions which lead to a superlinear dependence of the fluorescence intensity or photocurrent on the excitation density. On the assumption that the excitation density in our GaP-Zn crystals is proportional to the electrical current through the samples, and that a possible shift of the region of excitation with increasing current density has no influence on the brightness, we applied the Klasens analysis to the strongly superlinear behavior shown in Figs. 5 and 7. Experimental evidence made some simplification possible and then a complete analysis could be given.

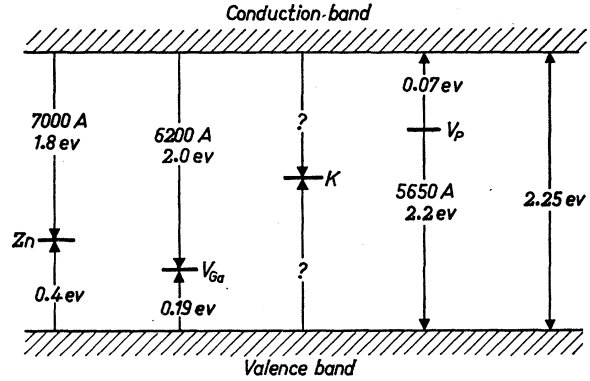


FIG. 12. Level scheme for GaP-Zn.

As a first simplification we will not consider the transitions via the level connected with V_{Ga} , because in GaP-Zn the emission via this level (6200 A, cf. Fig. 12) is always very weak.

The nomenclature used differs from the one given by Klasens⁶ mainly in this respect that the effective charge is indicated.¹⁰

- a = total density of the acceptors A caused by Zn,
- a^0 = density of the empty A levels,
- a^- = density of the occupied A levels,
- k = total density of the killer centers K (donor type),
- k^0 = density of the occupied K levels,
- k^+ = density of the empty K levels,
- d = total density of the donors D caused by P vacancies (donor type),
- d^0 = density of the occupied D levels,
- d^+ = density of the empty D levels,
- n = density of the free electrons,
- p = density of the free holes.

Using the above notation and the transitions $I, S, V, Q, E, B, F, U, C, L, T, W, R, G$ as indicated in Fig. 13,

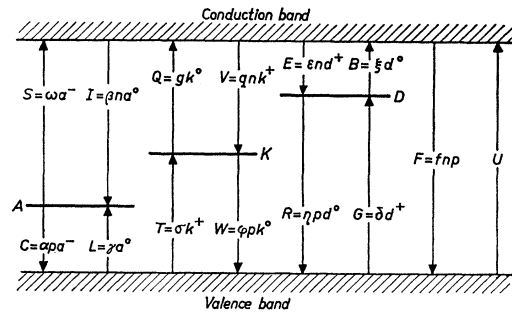


FIG. 13. The three-level (A , K , and D) model used in describing the recombination kinetics in GaP-Zn.

¹⁰ The suffix 0 means that the center has no effective charge, - that it has an effective negative charge, and + that it has a positive charge.

we can describe the stationary state in the most general case with the following equations:

$$dn/dt = S + Q + B + U - I - V - E - F = 0, \quad (1)$$

$$da^-/dt = 0 \quad \text{or} \quad C + S = L + I, \quad (2)$$

$$dd^+/dt = 0 \quad \text{or} \quad R + B = E + G, \quad (3)$$

$$dk^+/dt = 0 \quad \text{or} \quad W + Q = T + V, \quad (4)$$

the electric neutrality equation

$$p + d^+ + k^+ = n + a^-, \quad (5)$$

$$a = a^0 + a^-, \quad (6)$$

$$k = k^0 + k^+, \quad (7)$$

$$d = d^0 + d^+. \quad (8)$$

At zero current S , Q , B , and U are thermal electron generation processes. Already at small currents however, the injection of minority carriers (which can also be described by an excitation process U , because for each minority carrier an excess majority carrier is brought to the diffusion-recombination region to maintain charge neutrality¹¹) will exceed the thermal excitation transitions over large distances S and Q . By neglecting these transitions in Eq. (1) we get

$$U = I + V + F + E - B. \quad (1a)$$

If furthermore all other thermal excitation transitions (G, T) involving large activation energies are neglected in Eqs. (2)–(4) (Fig. 13) we get:

$$U = I + V + F + R, \quad (1b)$$

$$C = L + I, \quad (2a)$$

$$E = B + R, \quad (3a)$$

$$W = V. \quad (4a)$$

The eight equations (1b), (2a), (3a), (4a), (5), (6), (7), and (8) for the eight unknowns a^0 , a^- , k^0 , k^+ , d^0 , d^+ , n , and p , cover all possible situations for the three levels. Taking into account some of the experimental results, we shall further reduce the still vast number of possibilities.

In general recombination occurs both in the n -region and in the p -region. However, if the carrier-concentrations in both regions are largely different, the current in the region of recombination is essentially carried by the injection of minority carriers into the region with the weaker dope. In our case of Zn-doped GaP, we may expect the p dope to be much heavier than the n dope, and consequently we may assume a strong injection of holes into the n region. This means that electron-hole recombinations essentially take place in the n region. At zero excitation density and also with low currents, the acceptor levels in the n -region will be occupied and

therefore a in Eq. (6) will be equal to a^- . We further make the assumption that in our experiments the injection remains so low that $p \ll n$. Moreover k^+ is likely to be much smaller than d^+ . Then Eq. (5) becomes:

$$d^+ = a^- + n. \quad (5a)$$

Because the levels associated with the phosphorus vacancies are shallow, we will assume thermal equilibrium with the conduction band, which means that Eq. (3a) becomes

$$E = B. \quad (3b)$$

From (3b), with the use of (5a), (6a), and (8), we may calculate n . This gives:

$$n(n+a)/(d-n-a) = \xi/\epsilon = N_c \exp(-E_d/kT),$$

where ξ and ϵ are the characteristic constants governing the capture and release of electrons from the shallow donor level (Fig. 13). N_c is the density of states in the conduction band and E_d is the ionization energy of the donor level.

Thus $n = n_0(T)$ and is independent of U and is a function of temperature only. Since no luminescence is observed at small currents (Figs. 5–7) the electrons and holes at these excitation densities must essentially recombine via the killer centers (K) or via the band-band transition F . In contrast to GaN,¹ edge emission was not observed either with ultraviolet excitation or with excitation by injection of minority carriers, and therefore the band-band recombination F is also supposed to be radiationless. This assumption is supported by the fact that in GaP the minimum of the conductivity band is not at $k=0$.¹²

Since the luminescence efficiency also remains low at high current densities the major part of the recombination process will be radiationless. Consequently we can neglect I and R in Eq. (1b).

Our initial set of equations has now been simplified to

| | Code number | |
|------------------|-------------|------|
| $U = V + F,$ | 1,2 | (1c) |
| $C = L + I,$ | 1,2 | (2a) |
| $E = B,$ | 1 | (3b) |
| $W = V,$ | 1 | (4a) |
| $d^+ = a^- + n,$ | 1,2 | (5a) |
| $a = a^-,$ | 1 | (6a) |
| $k = k^0 + k^+,$ | 1,2 | (7) |
| $d = d^+,$ | 1 | (8a) |

where, following Klasens,⁶ the code numbers in the second column indicate which term is predominant [e.g., in Eq. (1) code number 1 means $U = V$ and code number 2 means $U = F$].

¹¹ F. H. Stieltjes and L. J. Tummers, Philips tech. Rundschau, **17**, 242 (1955).

¹² W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, J. Phys. Chem. Solids **11**, 339 (1959).

The number of possible situations is reduced to 16 and we shall see whether these conditions suffice to explain the experimental observations.

At low injections where $k=k_0$, we are left with a possible choice from the following 8 situations:

$$\begin{aligned} &1\ 1\ 1\ 1\ (1,2)\ 2\ 1\ 2, \\ &1\ 2\ 1\ 1\ (1,2)\ 2\ 1\ 2, \\ &2\ 1\ 1\ 1\ (1,2)\ 2\ 1\ 2, \\ &2\ 2\ 1\ 1\ (1,2)\ 2\ 1\ 2. \end{aligned}$$

In the fifth digit (1,2) both code numbers appear, because the choice of the code number in the fifth digit (1 or 2) does not influence the solutions of the variables we are interested in. From Eqs. (5a), (6a), and (8a) it can be seen that $d^+=d$, $a^-=a$, and $n=n_0$ and that all three are constant and independent of U .

In the situations represented by the first two sets, practically all injected holes are trapped by the K centers (transition W) and recombine radiationless with electrons from the conduction band (transition V). A simple calculation shows that

$$\begin{aligned} k^+ &= U/qn_0, & p &= U/\varphi k, & a^0 &= daU/\varphi k\gamma, \\ F &= fn_0U/\varphi k, & I &= \beta n_0\alpha aU/\varphi k\gamma, & R &= \eta en_0dU/\xi\varphi k, \\ & & C &= L = \alpha aU/\varphi k. \end{aligned}$$

All quantities are linearly proportional to U and as a consequence the only change in situation which can occur with rising current is by k^+ becoming equal to k , which means that the recombination via K gets blocked. This change occurs at $U_s = qn_0k$.

The new situations are now $1\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2$ and $1\ 2\ 1\ 1\ (1,2)\ 2\ 2\ 2$. In both situations p and k^0 are indefinite because only the product is given and equal to U_s/φ . Furthermore these situations exist only at a single value of $U = U_s = qn_0k$, which is a function of temperature.

This means (cf. also Klasens⁶) that p and k^0 change superlinearly and therefore both I and R rise superlinearly with current. The killer centers K are no longer active in the quenching process. Furthermore F also rises superlinearly.

A simple calculation shows that the situations represented by the remaining sets $2\ 1\ 1\ 1\ (1,2)\ 2\ 1\ 2$ and $2\ 2\ 1\ 1\ (1,2)\ 2\ 1\ 2$, where the recombination already essentially proceeds via F (band-band), both I and R remain proportional to U over the whole range of current. This shows at the same time that the low injection range cannot be described by one of these situations because then the superlinearity would not have arisen. These situations will therefore be left out of consideration.

With the superlinear cases $1\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2$ and $1\ 2\ 1\ 1\ (1,2)\ 2\ 2\ 2$ the next change can only be from $C = L$ to $C = I$ [$1\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2 \rightarrow 1\ 2\ 1\ 1\ (1,2)\ 2\ 2\ 2$], which has no effect on the behavior of p and k^0 , or from

$U = V$ to $U = F$, which means a change of the code number in the first digit leading respectively to $2\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2$ and $2\ 2\ 1\ 1\ (1,2)\ 2\ 2\ 2$. Either of the latter cases gives the proportionality of I and R with U experimentally observed. Situation $2\ 2\ 1\ 1\ (1,2)\ 2\ 2\ 2$ would, however, give the same temperature dependence for both I and R , which is not in agreement with experiment.

The changing conditions with rising excitation density thus can be appropriately represented by the following succession of situations:

$$\begin{aligned} 1\ 1\ 1\ 1\ (1,2)\ 2\ 1\ 2 &\rightarrow 1\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2 \rightarrow \\ &2\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2. \end{aligned}$$

It would need more detailed investigations to decide whether the succession of sets proposed is the only one possible. It is for example conceivable that a second killing level K' is present with a lower capture-cross section for capturing holes and that this level takes over from K when the latter gets blocked. In this case I and R would also rise superlinearly. The proposed succession predicts that both I and R rise at first linearly with the current, then superlinearly, and then again linearly. The superlinear part and the high-current linear part are actually observed (cf. Figs. 5-7). The low-current linear part is not observed, presumably because the luminescence intensity is too low in this region.

The proposed succession of sets also *quantitatively* explains the temperature shift of the superlinear range shown in Figs. 6-8. With the set $1\ 1\ 1\ 1\ (1,2)\ 2\ 2\ 2$ representing the superlinear range we find $U_s = qkn_0 \sim \exp(-E_d/kT)$.¹³ If we then plot the logarithm of the current i_s , at which the superlinearity occurs ($i_s = \text{const } U$) against T^{-1} , we should expect a straight line with a slope giving the donor-ionization energy E_d . Figures 14 and 15 show this plot for I and R . Straight lines are indeed obtained at low temperatures, the corresponding activation energy in both cases being 0.07 eV. This value of 0.07 eV agrees perfectly with the activation energy obtained from electrical measurements.³ Due to electron exhaustion, the lines in Figs. 14 and 15 level off at higher temperatures. This is just what one would expect because in our interpretation, the lines of Figs. 14 and 15 are essentially plots of the free-electron density against T^{-1} .³

The analysis given for GaP-Zn can also be applied for undoped GaP. The acceptor levels are in this case the Ga vacancies, and the corresponding I is the emission at 2.0 eV. Because in the superlinear range we again have $U_s = qkn_0$, one would expect to find similar curves as for GaP-Zn on plotting the logarithm of the current at which superlinearity starts versus T^{-1} .

Figure 16 indeed shows the exhaustion at higher temperatures. At lower temperatures the curve merges into a straight line from which again, an activation energy of

¹³ The exponent contains E_d/kT because in the n region the donors are partly compensated by acceptors.

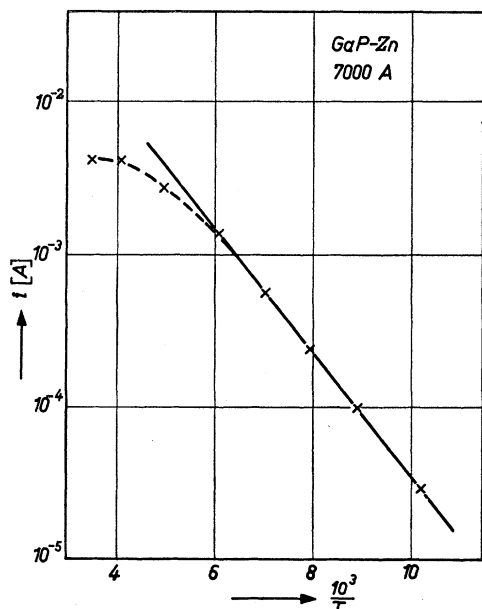


FIG. 14. Plot of $\log_{10} i_0$ against T^{-1} , where i_0 is the value of the current in the middle of the superlinear range of the curves in Fig. 6 (1.8-ev emission in GaP-Zn).

0.07 ev can be deduced. The reason why the saturation starts at lower U is attributed to a higher value of qk_0 in undoped GaP. Other experiments also point in this direction.

Similar investigations of the intensity of p - n luminescence as a function of current have been carried out

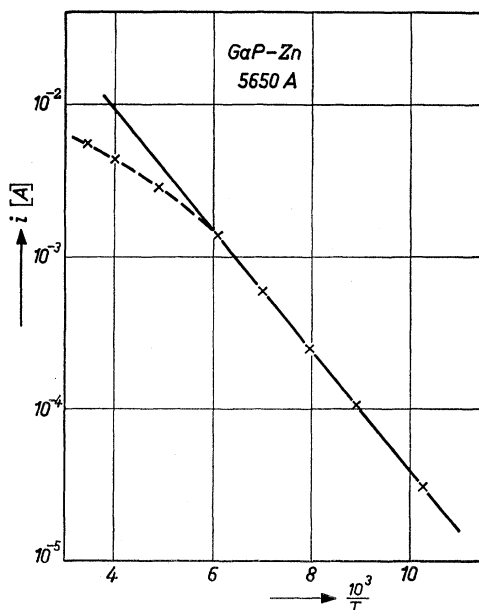


FIG. 15. Plot of $\log_{10} i_0$ against T^{-1} , where i_0 is the value of the current in the middle of the superlinear range of the curves in Fig. 7 (2.2-ev emission in GaP-Zn).

by Loebner and Poor.¹⁴ These authors found a quadratic relationship between I and i (current) for their green emission. There are reasons to believe that more than one green emission may occur in GaP.¹⁵

The analysis given also allows an interpretation of the temperature dependence of I and R in the high-current linear part.

In this region [set 2 1 1 1 (1,2) 2 2 2], one calculates

$$I = (\alpha/\gamma)(\beta a U/f) \quad \text{and} \quad R = (\epsilon/\xi)(\eta d U/f).$$

Because of the factors α/γ and ϵ/ξ , both I and R should depend on temperature. In the region of temperature quenching a plot of $\ln I$ and $\ln R$ versus T^{-1} should yield straight lines with slopes corresponding to the ionization energies of the acceptors (A) and the donors (D), respectively.

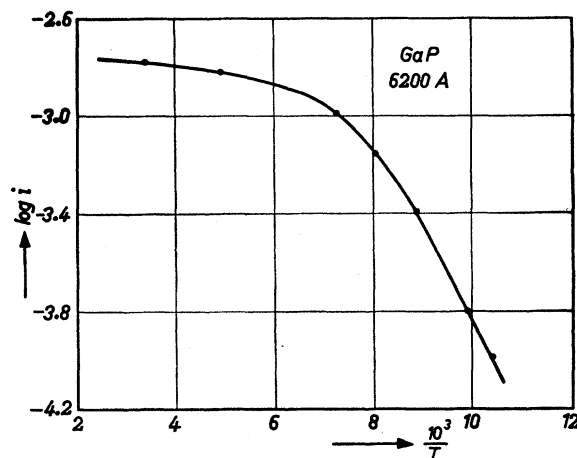


FIG. 16. Plot of $\log_{10} i_0$ against T^{-1} , where i_0 is the value of the current in the middle of the superlinear range of the curves in Fig. 8 (2.0-ev emission in GaP).

Straight lines are actually found, but only the calculated donor depth (0.07 ev) agrees quantitatively with the value deduced from conductivity measurements. The values found for the acceptor depths in GaP-Zn and undoped GaP however, are only about half as big as those electrically determined.

In any case the strong influence of the level depth on I and R is clearly comprehensible. The activation energy of the recombination centers should be high enough to avoid temperature quenching at the actual temperature of operation.

The intensity dependence of the photoluminescence given in Fig. 11 does not show any superlinearity. This is because the excitation densities in photoluminescence are much lower than in p - n luminescence. Assuming that with photoluminescence the set 1 1 1 1 (1,2) 2 1 2

¹⁴ E. E. Loebner and E. W. Poor, Phys. Rev. Letters **3**, 23 (1959).

¹⁵ Private discussion with Dr. Loebner.

applies, we calculate

$$I = (\alpha/\gamma)(\beta n_0 a U / \varphi k).$$

This means that I is proportional to U and further that I is a function of temperature. Both results agree with the experimental findings (cf. Fig. 11).

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Conduction Electrons in Pseudonickel Alloys from Hall Data*

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The two Hall coefficients and resistivity of four Ni—Cu—Fe alloys having 28 electrons per atom, with Ni content from 97 to 70 atomic percent, have been measured at 20°K, 77°K, and room temperature using fields up to 3.1 webers/meter². R_0 is found to increase with decreasing temperature for all compositions, and also to increase with decreasing Ni content for each of the three temperatures measured. The effective number of conduction electrons calculated from the R_0 's measured at low temperatures is found to fall smoothly from the anomalous peak at pure Ni to about 0.3 at 70% Ni, in agreement with the predictions of the four-band model. A short summary of the considerable evidence supporting this model is given. The extraordinary Hall coefficient, R_e , is negative at all temperatures for the three samples richest in Ni, being increasingly negative as the Ni content is lowered. On the other hand, the 70% Ni—20% Cu—10% Fe alloy has positive extraordinary Hall coefficients at all temperatures. The behavior of R_e obeys none of the variously proposed theoretical relations.

INTRODUCTION

A BAND model for explaining the ordinary Hall coefficients in alloys of the first transition group of elements has been introduced by Pugh.¹ This model, which was originally proposed by Mott² to account for the temperature dependence of the resistivity of Ni, has been singularly successful in predicting the magnitude and temperature dependence of the ordinary Hall coefficients as measured in a considerable number of different alloys.³⁻⁶ The predictions of this band model have been compared chiefly with data obtained in this laboratory, as data obtained in other laboratories is usually too incomplete to make these comparisons. This lack of completeness may be due to magnetic fields that are too small and/or cover too narrow a range for discriminating R_0 from R_1 , samples are too thin for ac-

curate measurements, or there is a failure to make measurements over a sufficiently wide range of temperatures.

The need for high accuracy and for covering a wide range of large magnetic fields stems from the fact that R_0 must be obtained from the relatively small slope of the ϵ_H (Hall field per unit sample current density) versus B curve (magnetic induction) at values of B large enough to assure that this slope is a straight line. That is, if M is the magnetization,

$$\begin{aligned} (\partial \epsilon_H / \partial B) &= R_0 + (R_1 - R_0)(\partial M / \partial B) \\ &= R_0 + R_e(\partial M / \partial B) = R_0^* \text{ by definition.} \end{aligned} \quad (1)$$

Thus R_0^* , the slope of the ϵ_H versus B curve, is the same as R_0 only where $R_e(\partial M / \partial B)$ is negligible. Even at very low temperatures, this latter term may be slow to approach negligible values as B is increased. Values for R_0 obtained with fields between 1 and 2 webers/meter² (10 to 20 kgauss) are often completely unreliable. Near Curie temperatures, the term $R_e(\partial M / \partial B)$ remains comparable with R_0 to the largest fields obtainable in this laboratory, about 3.2 webers/meter².

The alloys of Ni containing about 20 to 50% Cu or 30 to 80% Co have R_0 's at temperatures far below their Curie temperature that correspond to approximately 0.3 conduction electron per atom. This agrees with predictions of the band model, since only half of the 4s electrons, the half with spins parallel to the field, have mobilities large enough to affect the measurement. Furthermore, measurements upon the temperature

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[‡] Submitted by A. C. Ehrlich in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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² N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).

³ A. I. Schindler and E. M. Pugh, Phys. Rev. **89**, 295 (1953).
S. Foner, F. E. Allison, and E. M. Pugh, *ibid.* **109**, 1129 (1958).
F. E. Allison (unpublished data on Ni₂Mn).

⁴ S. Foner and E. M. Pugh, Phys. Rev. **91**, 20 (1953).

⁵ F. E. Allison and E. M. Pugh, Phys. Rev. **102**, 1281 (1956).

⁶ P. Cohen, thesis, Carnegie Institute of Technology, 1955 (unpublished).

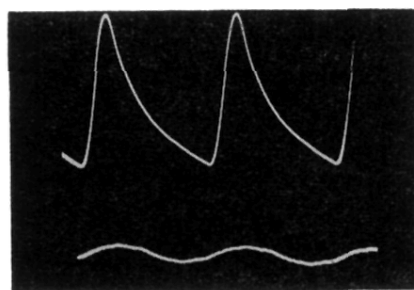


FIG. 2. p - n luminescence with excitation by alternating current.
Upper curve: luminescence (current in CdS cell) versus time.
Lower curve: voltage versus time (GaP-Zn).