

63-3-3

ELECTRON INJECTION LASER

Report No. 3/Contract DA-36-039-SC-90711

CATALOGED BY ASTIA

S AD NO

403130

403 130

3RD QUARTERLY PROGRESS REPORT

1 DEC., 1962—28 FEB., 1963

INTERNATIONAL BUSINESS MACHINES CORP.

Thomas J. Watson Research Center, Yorktown Heights, New York

RECEIVED
JAN 10 1963
U.S. ARMY
SIGNAL RESEARCH AND DEVELOPMENT
LABORATORY
FORT MONMOUTH, NEW JERSEY

Work Performed for U.S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

ASTIA AVAILABILITY NOTICE: Qualified Requestors May Obtain
Copies of this Report from ASTIA. ASTIA Release to OTS Not Authorized.

UNCLASSIFIED

ELECTRON INJECTION LASER

Report No. 3
Contract DA-36-039-SC-90711

Third Quarterly Progress Report

1 December 1962 to 28 February 1963

Program Objective: The object of this research program is to find an electron injection laser.

Report Prepared by

R.W.Keyes, G.J.Lasher, K. Weiser

TABLE OF CONTENTS

Purpose	3.
Abstract	4.
Publications, Lectures, Reports and Conferences	5.
Factual Data	
Part I. Indium Phosphide	
A. Indium Phosphide Technology.	6.
B. Electroluminescence of Indium Phosphide Diodes.	8.
Part II. Double Diffused (Zn-Mn) GaAs Diodes.	17.
Part III. The Diffusion of Zinc into GaAs.	19.
Part IV. Spontaneous and Stimulated Line Shapes in Semiconductor Lasers.	32.
Conclusions	37.
Program for Next Interval	38.
Identification of Key Personnel	39.
Abstract Cards.	

3.

PURPOSE

The purpose of this contract is the development of improved electron injection lasers. The problem is being attacked by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.

ABSTRACT

Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission (narrowing of the emitted line by a factor of 1.5) has been observed in some of the diodes at high current densities.

The electroluminescence of double diffused (Zn-Mn) GaAs diodes has been investigated at high currents. No line narrowing was observed.

The nature of p-n junctions in GaAs lasers is influenced by the anomalous nature of zinc diffusion in GaAs. The concentration dependence of the zinc diffusion constant in GaAs is known to be of the form $D \sim ac^2$ where c is the concentration of zinc. This behavior suggests a substitutional-interstitial mechanism for diffusion. The magnitude of the proportionality constant a and its temperature dependence have been compared with Theory. The comparison provides strong evidence for the substitutional-interstitial diffusion mechanism.

Calculations of the line shapes of spontaneous and stimulated emission in semiconductors have been carried out. Parabolic bands are assumed. The theory predicts that the stimulated emission spike appears at a frequency close to the maximum of the spontaneous emission.

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES.

Dr, K. Weiser presented a talk "Radiative Recombination from InP p-n Junctions" at the New York Meeting of the American Physical Society on January 26th, 1963. An abstract was published (with R. S. Levitt) in Bull. Am. Phys. Soc. 8, 29 (1963).

Dr. G. Lasher's paper "Threshold Relations and Diffraction Loss for Injection Lasers" was published in the IBM Journal of Research and Development, Vol. 7, No. 1, p. 58 (January 1963).

The following patent disclosures were submitted:

W.P. Dumke and K. Weiser - Double Diffused Laser Structure
November 1, 1962.

K. Weiser, R. S. Levitt and W.P. Dumke - Light Emitting Diodes
with Negative Resistance. December 4, 1962.

K. Weiser - Use of Surface Layers of GaAs-GaP for Reducing
Threshold Current for Lasers. December 5, 1962.

R.S. Levitt - K. Weiser - Rapid Switching of Bistable Negative
Resistance Diodes with Non-destructive Readout. Feb. 11, 1963.

K. Weiser - R.S. Levitt - Semiconductor Light Amplifier.
February 11, 1963.

R.S. Levitt - K. Weiser - P-Si-NP Photon Coupled Device.
February 19, 1963.

R.S. Levitt - K. Weiser - Fabrication of P-Si NP Device.
February 19, 1963.

6.

I. INDIUM PHOSPHIDE.

A. Indium Phosphide Technology.

In the second Quarterly Report we gave some details on the preparation and spectral output of InP diodes. We wish to recapitulate briefly some of the salient features, and add some details. We prepare diodes by diffusing zinc into n-type material (carrier concentration 10^{17} to 10^{18} cc^{-1}) at about 750°C for two hours. The junction depth achieved in this manner is approximately two mils. As mentioned before, the electrolytic KOH etching technique commonly employed for GaAs does not reveal junctions in InP, and we have not yet found a really foolproof method for detecting them. The best technique found so far is to use electrolytic etching with dilute HF (appr. 1%), for a period of a few seconds. To fabricate our diodes, we cleave parallel wafers of typical dimensions shown in Fig. 1, where we also show details of the contact methods which will be described below.

Around the beginning of the period we discovered that the electrical characteristics of diodes, as initially prepared, deteriorated at current densities above about 10^4 amps/cm^2 at 77°K . At higher current densities the i-V characteristics lost the sharp rectangular shape of good diodes, and eventually either became linear or else the diodes opened up. During the deterioration of the

7.

diodes the light output saturated rather than increasing linearly with current. It was therefore impossible to expect the onset of stimulated emission until the deterioration could be prevented in the current range where "lasing" might be expected.

The deterioration turned out to be due to faulty contacts on the p-side. (Satisfactory, low resistance contacts ($R \sim 1 \Omega$) are easily made on the n-side by alloying it to tin-clad tabs.) Therefore, we have concentrated on attempts to solve the contact problem on the p-side. Initially, following common usage in GaAs, we used indium dots for alloying to the p-side. We found, however, that this procedure gave rectifying, high resistance contacts ($R > 10 \Omega$). We believe that the high resistance at the contacts produced local heating which resulted in decomposition of the material. In many instances, streaks of indium along the sides were actually visible after the deterioration of the i-V characteristics.

We can summarize our efforts to make low resistance contacts to p-type InP as follows: Indium, lead or tin dots on p-InP are totally unsatisfactory even when admixed with zinc or cadmium. Gold-antimony clad tabs can be used to make an improved contact giving a contact resistance between five and seven ohms. Silver plating was satisfactory from the point of view of resistance ($R \sim 2 \Omega$)

8.

but tended to peel off, and was therefore impractical. The most satisfactory results are obtained by the following procedure.

Approximately 1μ layers of cadmium and gold are evaporated onto the sample. This is followed by alloying for a few seconds. A low resistance region to which a cadmium dot can easily be alloyed is produced. An excellent contact of low resistance ($R \sim 1\Omega$) resulted. The i-V characteristic is shown in Fig. 2. Almost equally satisfactory contacts (1 to 2Ω resistance) can be produced by directly alloying cadmium on to the p-layer. A tin-coated wire can then be soldered to the cadmium dot. We have not yet progressed to the point where the fabrication of low resistance units with good i-V characteristics is a routine process but we believe that we are close to this point. When the contact resistance is two ohms or less we can pass currents up to twenty amperes (100 nsec pulses, repetition rate 100 cps) through these diodes without affecting them adversely.

B. Electroluminescence of Indium Phosphide Diodes.

The improvements in Indium Phosphide technology detailed above permit the passage of high currents through the diodes. Consequently, a much more thorough study of their electroluminescence has become possible. As discussed in the second Quarterly Report, the spontaneous emission in most diodes occurs at about

.960 μ at 300°K and .905 μ at 77°K with a line width of about 150 Å .

In the most heavily doped materials studied where the carrier concentration on the n-side was of the order of $3 \times 10^{18} \text{ cc}^{-1}$ a shift to longer wave length occurs with increasing current, and the line narrows from an initial width of over 200 Å to about 150 Å . These effects are illustrated in Figures 3a and 3b. A shift to shorter wave length is observed in all diodes but becomes easily observable only where the substrate is heavily doped. This effect has been reported in GaAs,⁽¹⁾ and has been observed by us in that material too. Its origin probably lies in a shift in bandgap in heavily doped material due to a "tailing" of the conduction band which is easily filled as the injection level increases. We also wish to call attention to the fact that the temperature dependence of the emission intensity is much more pronounced in InP than in GaAs as illustrated in Fig. 4. We do not know whether the difference is the result of a difference in quantum efficiency above 77°K or whether it is caused by a different temperature dependence of the absorption constant. At liquid nitrogen temperature the intensity of light emitted by the best InP diodes equals that of low threshold lasing GaAs diodes.

With the improved contacts it is possible to study the light emission of diodes at current densities up to about $4 \times 10^5 \text{ amps/cm}^2$. We have concentrated on the study of diodes made from three crystals

which we shall designate by A, B and C. Carrier concentrations in these crystals were about 2, 7 and $30 \times 10^{17} \text{cc}^{-1}$ respectively. The light output from diodes made from crystal A is comparable to that from low threshold GaAs lasers from about 10ma up. Crystals B and C, on the other hand, produced diodes with considerably less light output; furthermore, the light intensity was superlinear with current up to about 100ma. We do not know whether this behavior is characteristic of heavily doped InP. In diodes made from crystals B and C we observed no line narrowing (other than the initial narrowing to about $150 \text{ \AA}$, which was discussed earlier in connection with Fig. 3 and which is attributed to a band structure effect). In four diodes from crystal A, however, we did observe line narrowing from an initial line width of about $150 \text{ \AA}$ (at currents of about 1 ampere) to about $90 \text{ \AA}$ at currents from 9 to 14 amperes depending on the unit. We show the results for one of these units in Fig. 5. We attribute this line narrowing at high currents to stimulated emission. The contact resistance in these diodes was still sufficiently high so that we were not able to pass more current through to see whether further line narrowing occurred.

- (1) J. Pankove - Phys. Rev. Letters 9, 283 (1962).

11.

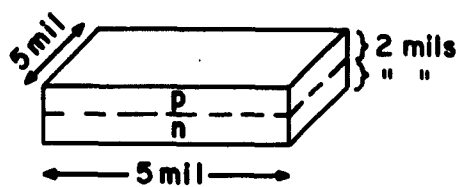
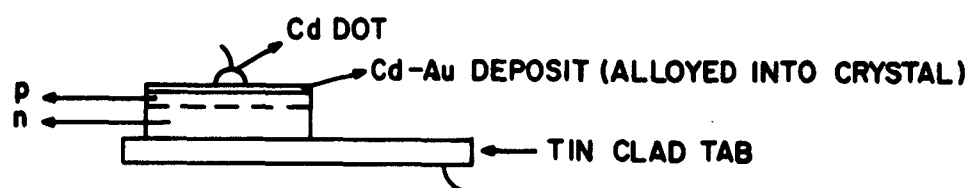


Fig. 1 Geometry of the laser structure

12.

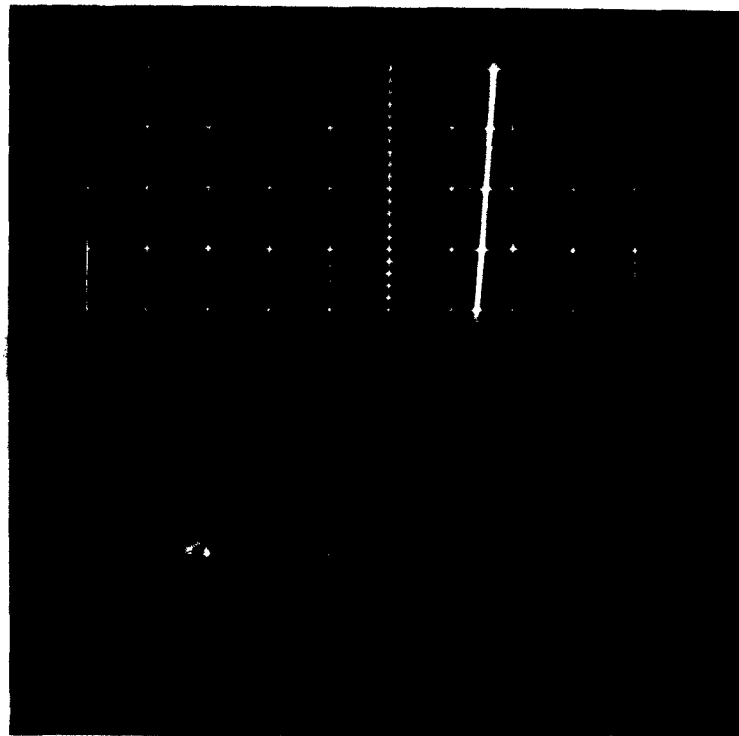


Fig. 2 I - V Characteristics of InP Diode at 77 K. Contact on n-side: tin clad tab; contact on p-side: Cd-Au alloy deposited and alloyed with Cd dot alloyed on top. Horizontal scale - 1 volt/cm; vertical scale - 50 milli-amp/cm.

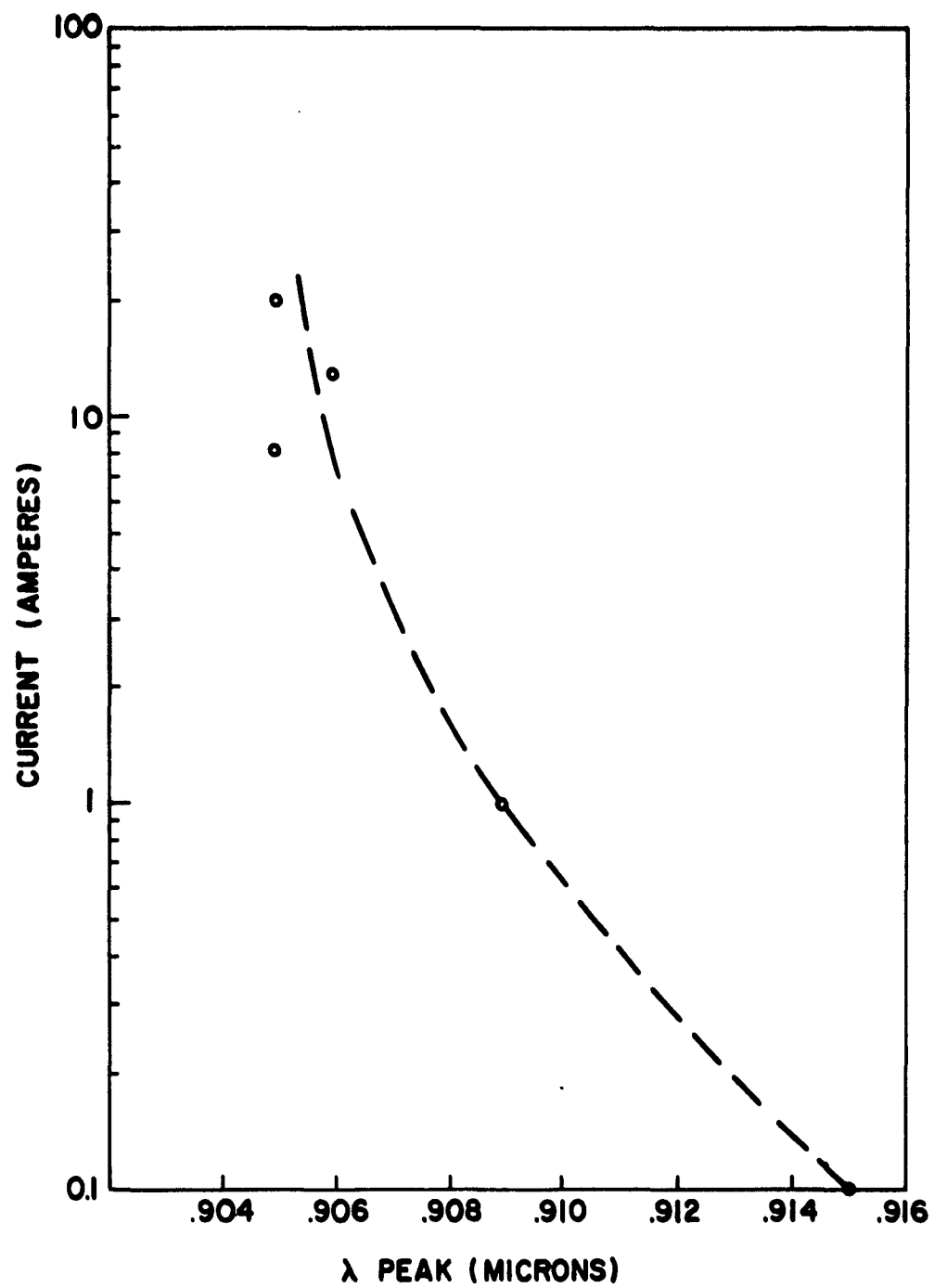


Fig. 3a Peak emission wavelength vs current for an InP diode

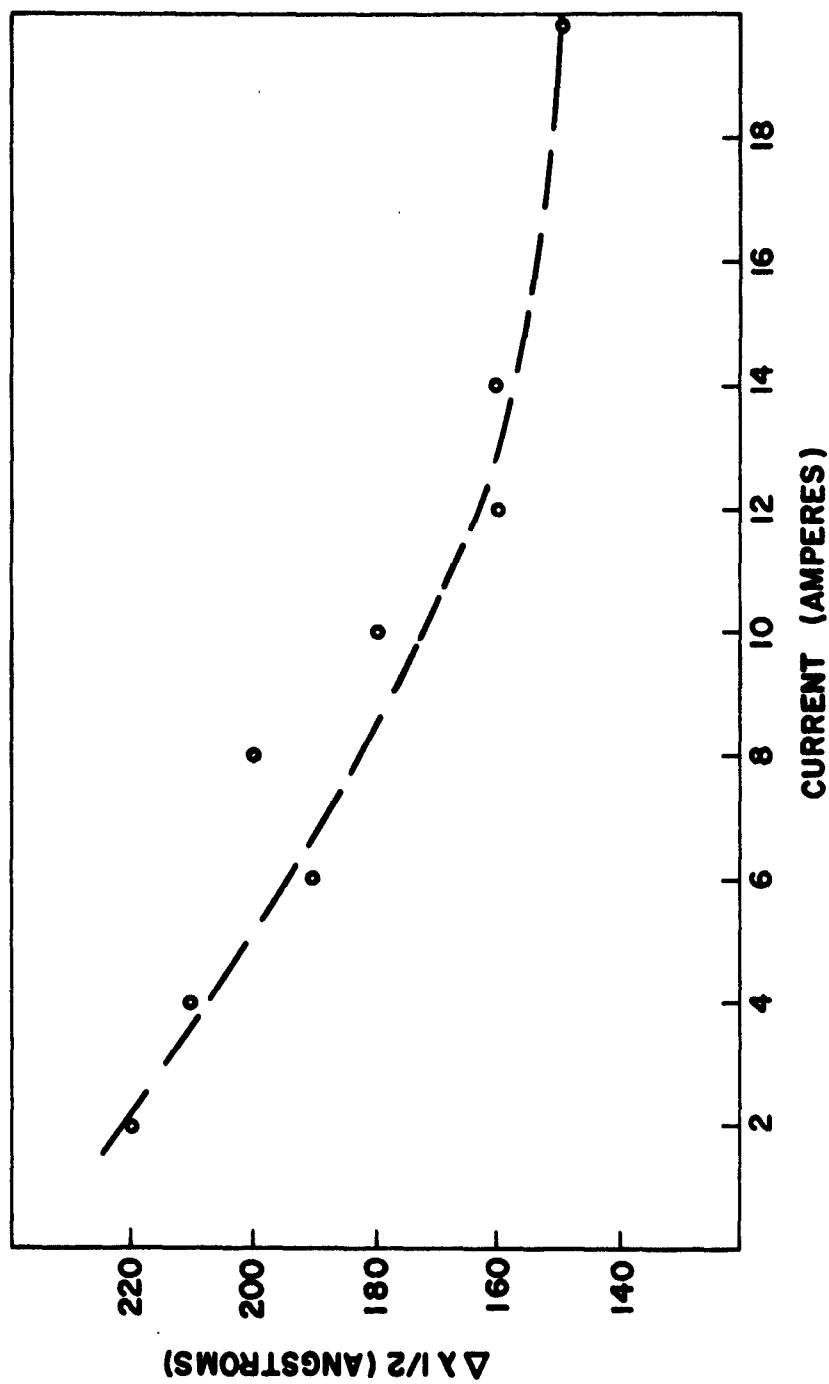


Fig. 3b Line width vs current for an InP diode

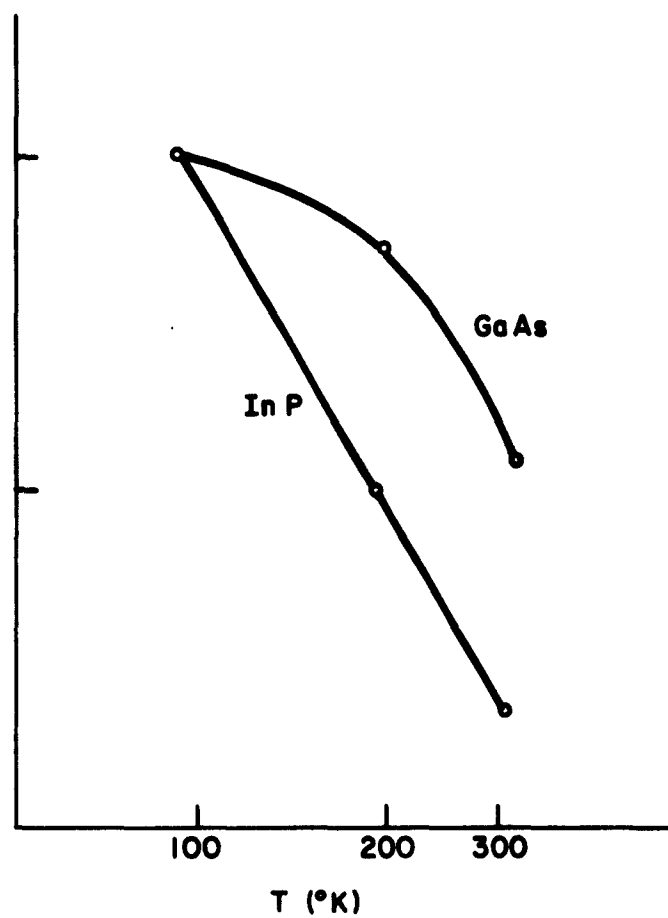


Fig. 4 Electro-luminescent efficiency of InP and GaAs
(in arbitrary units normalized to have the same value at 77°K)

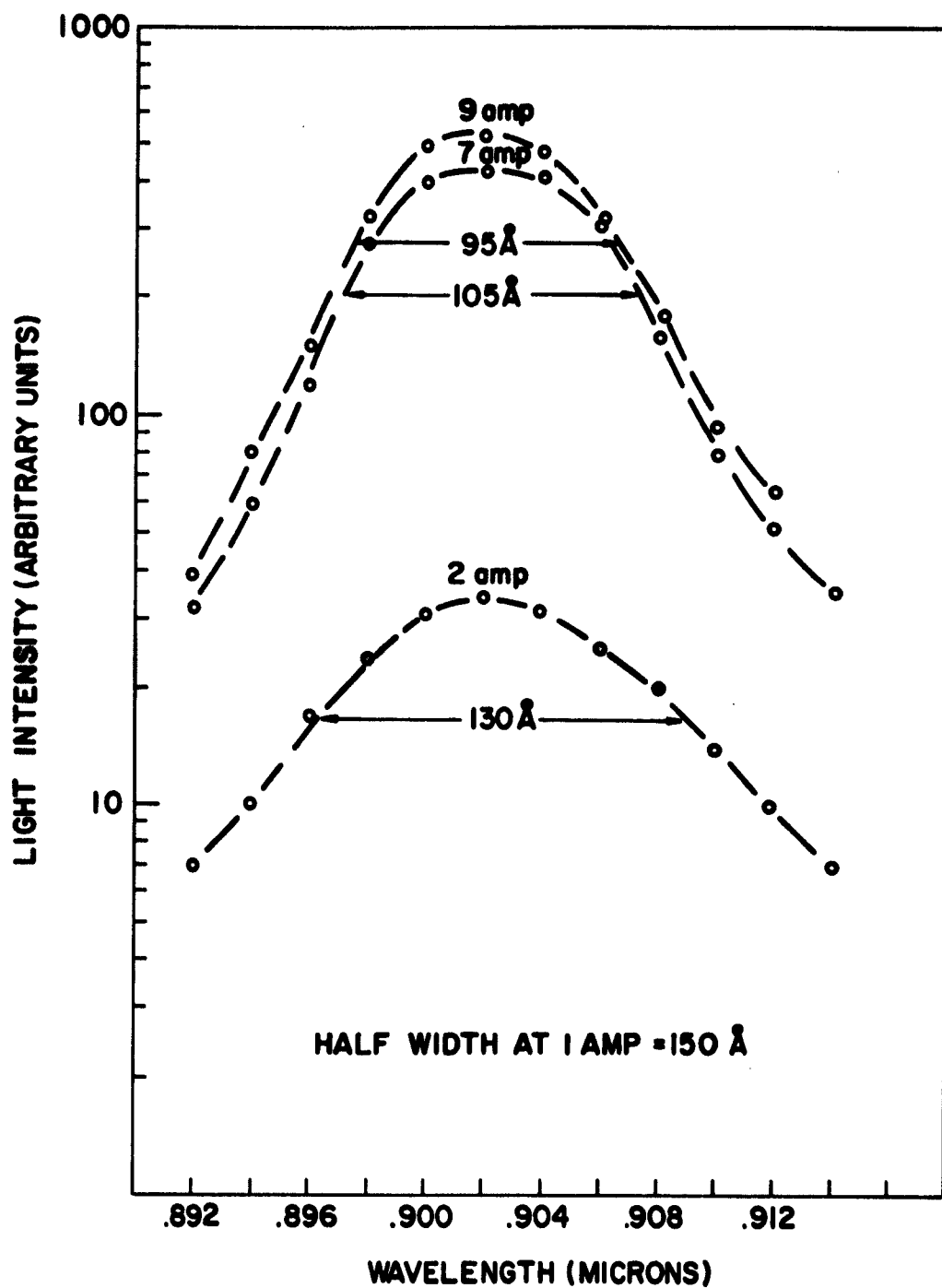


Fig. 5 Line Narrowing Exhibited by One Sample InP Diode

II. DOUBLE DIFFUSED (Zn-Mn) GaAs DIODES.

In the second Quarterly Report we described some of the interesting electrical and optical properties of diodes made by diffusing zinc and manganese into n-type material. We have investigated the possibility of switching these diodes from a low current ("pre-breakdown") condition into a conducting state of sufficiently high current where lasing might be expected. Since electron-hole recombination through manganese centers is less likely than recombination through zinc centers one would expect stimulated emission through the latter, if at all. So far we have seen no line narrowing in the units we have investigated, even at current densities of the order of 10^5 amps/cm². We believe that the reason lies in the much greater width of the light emitting region in these diodes than is found in normal GaAs diodes. In normal diodes the width of the light emitting region is of the order of microns.⁽¹⁾ In the Zn-Mn diodes the width was investigated by other workers in this laboratory who found the following picture: Before the onset of the negative resistance light is emitted in a narrow ribbon about 10μ wide at a distance of about 60μ from the junction. In the postbreakdown region, where lasing might occur, the light-emitting region sweeps back to the junction so that the total width of the light emitting region is about 70μ .

Thus the photon density at high currents is much less than in ordinary diodes, and the threshold current for lasing should be greatly increased.

- (1) A.E. Michel and E.J. Walker, M. I. Nathan, IBM Journal 7, 70 (1963).

III. THE DIFFUSION OF ZINC INTO GaAs.

It was reported by Cunnell and Gooch⁽¹⁾ that the diffusion of zinc in gallium arsenide does not follow a complementary error function curve but is rather characterized by a fast diffusion near the surface and a very slow diffusion in the interior of the crystal where the zinc concentration is low. This behavior was confirmed by Goldstein⁽²⁾ who contributed the additional observation that normal diffusion does take place at low temperatures (below about 800°C) if the zinc concentration is kept sufficiently low. Cunnell and Gooch⁽¹⁾, Allen,⁽³⁾ and Kendall⁽⁴⁾ all have realized that the explanation for the anomalous diffusion lies in a concentration dependence of the diffusion constant. Indeed, Cunnell and Gooch found that D is proportional to $c^{1.75}$ at 1000°C over the concentration range from about 1 to $4 \times 10^{19} \text{ cc}^{-1}$. Kendall has made a similar analysis over a wider concentration range at 900°C. We present his data in Fig. 1 where we have also included four points based on the data of Cunnell and Gooch⁽¹⁾ at that temperature. It is seen that D is approximately proportional to c^2 . The same conclusion has been reached by Weisberg and Blanc.⁽⁵⁾ A concentration dependence of this nature suggests that the diffusion of zinc is of the dissociative type involving the simultaneous diffusion of substitutional and interstitial zinc, as will be explained below. This

suggestion was first made by Longini,⁽⁶⁾ and has also been made by Kendall⁽⁴⁾ and by Weisberg and Blanc.⁽⁵⁾ It is the purpose of this note to examine this suggestion critically. As will be shown below, the proportionality constant of the relation $D \sim ac^2$ involves the diffusion constant of the interstitial species and the ratio of interstitial to substitutional impurity atoms. We wish to see whether the magnitude of the proportionality constant and its temperature dependence are what one may expect on the basis of what is known experimentally and theoretically about interstitial impurities in the diamond lattice.

According to the theory of diffusion for this mechanism as first developed by Frank and Turnbull⁽⁷⁾ for copper in germanium, the total diffusion constant D_{tot} is given by:

$$D_{\text{tot}} = D_i \frac{c_i}{c_i + c_s} \quad (1)$$

where D_i is the diffusion constant of the interstitial species, c_i the concentration of the interstitial species and c_s that of the substitutional species. The only requirement for Eq. (1) to hold is that a) $D_i \gg D_s$, the diffusion constant for the substitutional species, and b) the dislocation concentration is high enough so that there is a ready supply of vacancies in the crystal to replenish those which are used up in the conversion of interstitial to substitutional atoms. Unless $D_{\text{tot}} \sim D_i$, $c_i \ll c_s$

so that we can neglect c_i in the denominator of Eq. (1). In the case of interest D_{tot} is of the order of 10^{-8} or smaller, while D_i is of the order of 10^{-4} as will be discussed below, so that c_i is indeed much smaller than c_s . According to the theory of Longini and Greene⁽⁸⁾ the ratio c_i/c_s can be expressed as:

$$\left(\frac{c_i}{c_s}\right) \approx \left(\frac{c_i}{c_s}\right)_0 \left(\frac{c_{\text{tot}}}{n_i}\right)^2 \approx \left(\frac{c_i}{c_s}\right)_0 \left(\frac{c_s}{n_i}\right)^2 \quad (2)$$

The quantity $\left(\frac{c_i}{c_s}\right)_0$ is the ratio of interstitial to substitutional zinc in intrinsic material where the carrier concentration is n_i . Also, it is assumed that the interstitial species is a single level donor and the substitutional species a single level acceptor.

Combining Eqns. (1) and (2), yields:

$$D_{\text{tot}} = D_i \left(\frac{c_i}{c_s}\right)_0 \left(\frac{c_s}{n_i}\right)^2 \quad (3)$$

The applicability of this equation extends over only a limited range of concentrations. First of all, as discussed by Longini and Greene,⁽⁸⁾ we must have $c_s \gg n_i$. At the same time, however, classical statistics should be obeyed. Furthermore, when the factor multiplying D_i begins to approach unity then D_{tot} must approach D_i , and hence must become independent of c_s . At low values of c_s , D_{tot}

must again become independent of c_s since it must approach D_s . Over a limited concentration range D_{tot} should however be proportional to c^2 , and hence the experimental data of Fig. 1 suggest that the diffusion mechanism is of the substitutional-interstitial dissociative type. Such a concentration dependence is not convincing evidence, however, since some other mechanism may lead to a similar concentration dependence. We must therefore examine the magnitude and the temperature dependence of $D_i \left(\frac{c_i}{c_s} \right) / n_i^2$.

From Fig. 1 we find that $D_i \left(\frac{c_i}{c_s} \right) / n_i^2$ is approximately equal to 1×10^{-48} . We estimate n_i^2 to be equal to 2×10^{34} at 900°C , using the following parameters to calculate it: The band gap is taken as $(1.56 - 4.2 \times 10^{-4} T)$ ev.⁽⁹⁾ The valence band effective mass is taken to be $0.5m_0$.⁽⁹⁾ The conduction band effective mass at $k = 0$ is taken to be $.072m_0$.⁽⁹⁾ The relative contribution of the conduction band minima away from $k = 0$ is taken as $70 e^{-.36/kT}$, as proposed by Ehrenreich.⁽¹⁰⁾ We find that the contribution of these minima to the number of thermally available states in the conduction band is about twice as large as the contribution of the minimum at $k = 0$. Finally, we find that $D_i (c_i/c_s)$ equals $1.5 \times 10^{-16} \text{ cm}^2/\text{sec}$.

We now make the assumption that D_i for Zn^+ is approximately the same as D_i for Cu^+ . This assumption is buttressed by

calculations by Pauling⁽¹¹⁾ which yield an ionic radius for Zn^+ equal to $0.88 \text{ \AA}$ while that for Cu^+ equals $0.96 \text{ \AA}$. No experimental verification of these radii seems to exist, and we shall accept them as a postulate. According to the theory of interstitial diffusion proposed by the author⁽¹²⁾ such a small difference in ionic radii should lead to a negligible difference in diffusion constants. We shall therefore take D_i as about $1.5 \times 10^{-4} \text{ cm}^2/\text{sec}$, which is the diffusion constant for interstitial copper in GaAs as determined by Hall and Racette.⁽¹³⁾ Combining this estimate of D_i with the above value for $D_i(c_i/c_s)$ gives

$$\left(\frac{c_i}{c_s} \right)_0^{\text{Zn}} \sim 1 \times 10^{-10} \text{ (based on analysis of diffusion data)} \quad (4)$$

Before proceeding further, we wish to point out that while this ratio of interstitial to substitutional zinc in intrinsic material is negligibly small, it rises to about 10^{-4} at a zinc concentration of 10^{20} cc^{-1} at 900°C .

We now wish to examine whether the ratio of $(c_i/c_s)_0$, thus calculated, is reasonable in the light of what is known about interstitial solubilities. We draw on experimental data on interstitial copper in GaAs as determined by Hall.⁽¹³⁾ According to the theory of interstitial solubility proposed by the author⁽¹⁴⁾ the concentration ratio of interstitial zinc to interstitial copper would be $\exp(-\Delta(I.P.)/kT)$ provided that the zinc and copper reservoirs from which the atoms are placed

into the interstitial positions are at the same chemical potentials.

Δ (I. P.) is the difference in ionization potential of the free atoms of zinc and copper. We assume again, of course, that the ionic sizes of copper and zinc are closely similar so that the repulsive energy contribution to the heat of solution is about the same for the two impurities. We thus obtain

$$\left(\frac{c_i}{c_s}\right)_o^{\text{Zn}} = \left(\frac{c_i}{c_s}\right)_o^{\text{Cu}} \exp[\text{I. P. (Cu)} - \text{I. P. (Zn)}]/kT \exp \Delta E_s/kT \quad (5)$$

We must now estimate the term $\exp \Delta E_s/kT$ which corrects for the difference in the chemical potential of substitutional zinc and substitutional copper. The symbol ΔE_s stands for the difference in energy between placing a zinc atom into a substitutional site from a solid zinc reservoir and the energy to carry out the same process for a copper atom from a solid copper reservoir. We can estimate this term from the ratio of maximum solubilities of substitutional zinc and copper on the basis of the following considerations: At the maximum solubility at a given temperature the increase in free energy of the host crystal equals the decrease in free energy of the melt since solid and molten GaAs are then in equilibrium. If the melt is ideal the depression of the melting point is a function of the impurity

content of the melt only. Hence, the concentration of zinc and copper in the melt would be the same. GaAs melts are essentially ideal with respect to excess gallium and arsenic.⁽¹⁵⁾ No liquidus curves exist for Cu-GaAs or Zn-GaAs but it seems reasonable to assume that these systems too are fairly ideal or at least exhibit similar deviations from ideality. Certainly in germanium and silicon melt the deviations from ideality are rather small.⁽¹⁶⁾ Assuming ideal melts and therefore equal concentrations of zinc and copper in the melt, we find that $(c_s^{Cu}/c_s^{Zn})_{\max} = \exp - (\Delta H_f - \Delta E_s)/kT$. The new symbol ΔH_f is the difference in heats of fusion of copper and zinc. We find that $\exp \Delta E_s/kT = 2 \times (c_s^{Cu}/c_s^{Zn})_{\max}$.

We substitute for $\exp \Delta E_s/kT$ in Eq. (5), and find

$$\left(\frac{c_i}{c_s}\right)_o^{Zn} = \left(\frac{c_i}{c_s}\right)_o^{Cu} \cdot 2 \left(\frac{c_s^{Cu}}{c_s^{Zn}}\right)_{\max} \exp \Delta(I.P.)/kT \quad (6)$$

At 900°C, Hall and Racette found a value of 6×10^{-3} for $(c_i/c_s)_o^{Cu}$.⁽¹³⁾ The ratio $(c_s^{Cu}/c_s^{Zn})_{\max}$ as determined from the investigation of copper solubility by Fuller and Whelan,⁽¹⁷⁾ and zinc solubility by Kendall,⁽⁴⁾ equals 3×10^{-3} . Using values of ionization potential from the literature we find $\left(\frac{c_i}{c_s}\right)_o^{Zn} = 2 \times 10^{-12}$ (based on solubility data for copper, and theory).⁽⁷⁾

The ratio thus calculated is lower by a factor of fifty, than the value obtained from an analysis of the zinc diffusion data. (Eq. 4) In view of the fact that these calculations involve a number of exponential quantities the agreement is quite satisfactory.

We now inquire into the temperature dependence of the diffusion constant. According to Eq. (3) the temperature dependence should be of the form $D \propto e(-\Delta E_{\text{diff}}/kT)$, where

$$\Delta E_{\text{diff}} = \Delta E_{D_i} + \Delta E_{\text{subst-interst.}} - E_g \quad (8)$$

ΔE_{D_i} is the activation energy for diffusion of interstitial zinc, $\Delta E_{\text{subst-interst.}}$ is the energy needed to transfer a zinc atom from a substitutional to an interstitial site in intrinsic material, and E_g is the band gap of GaAs at 0°K. We use $\Delta E_{\text{diff}} = 0.52$ ev as determined by Hall and Racette for interstitial copper,⁽¹³⁾ and $E_g = 1.56$ ev.⁽⁹⁾ We estimate $\Delta E_{\text{subst-interst.}}$ from $(c_i/c_s)_0 \sim \exp(-\Delta E_{\text{subst-interst.}}/kT)$ which yields a value of 2.3 ev. Thus $\Delta E_{\text{diff}} \sim .53 + 2.3 - 1.56 = 1.3$ ev. In Fig. 2 we show that the experimental value of ΔE_{diff} equals 1.6 ev, in fairly good agreement with our calculated value. If, for $(c_i/c_s)_0$, we chose the value given in Eq. (7) we find $\Delta E = 1.7$ ev, which is in even better agreement with experiment. This value for ΔE should be compared to the value found by Goldstein⁽²⁾ at lower temperatures and concentrations where normal, i.e. concentration independent behavior was

observed. Goldstein found $\Delta E = 2.43$ ev in close agreement with the value he found for cadmium. Presumably, this energy corresponds to a pure substitutional diffusion. The values for D in the temperature range reported by Goldstein seem rather high. Assuming that he observed pure substitutional diffusion, it is hard to see how he could observe diffusion constants which are larger than those observed under conditions of a concentration dependent diffusion constant.

In further support of the substitutional interstitial mechanism we wish to point out that we have diffused zinc into manganese doped GaAs and found a markedly enhanced diffusivity.⁽¹⁸⁾ This behavior also supports the picture that a substitutional-interstitial mechanism is at play. The presence of Mn (an acceptor) should increase the ratio c_i/c_s and thus increase the diffusion constant (See Eq. (1)). Indeed, the most convincing evidence for the validity of the mechanism proposed should come from a study of the solubility and diffusivity of zinc in heavily doped p-type material as was done by Hall and Racette⁽¹³⁾ for copper in various materials. It is also known that the dislocation density has a pronounced effect on this mechanism,⁽¹⁹⁾ and hence diffusion studies in crystal with different dislocation densities should be a critical test of the mechanism proposed.

ACKNOWLEDGMENTS.

We appreciate D.L. Kendall's (Stanford University) permission to use the data shown in Fig. 1 and 2 prior to publication. It is also a pleasure to acknowledge a number of stimulating discussions with H. Rupprecht of this laboratory. Finally, we appreciate R.W. Keyes' careful reading of the manuscript.

REFERENCES

- (1) F.A. Cunnell and C.H. Gooch, J. Phys. Chem. Solids 15, 127 (1960)
- (2) B. Goldstein, Phys. Rev. 118, 1024 (1959)
- (3) J. W. Allen, J. Phys. Chem. Solids 15, 134 (1960)
- (4) D.L. Kendall, Stamford University; to be published.
- (5) L.R. Weisberg and L. Blanc, RCA Laboratories, personal communication.
- (6) R.L. Longini, Solid State Electronics 5, 127 (1962)
- (7) F.C. Frank and D. Turnbull, Phys. Rev. 104, 617 (1956)
- (8) R.L. Longini and R.F. Greene, Phys. Rev. 102, 992 (1956)
- (9) C. Hilsum and A.C. Rose-Innes, Semiconducting III-V Compounds, Pergamon Press, 1961.
- (10) H. Ehrenreich, Phys. Rev. 120, 1951 (1960)
- (11) L. Pauling, Nature of the Chemical Bond, Cornell (1960) (3rd ed.)
- (12) K. Weiser, Phys. Rev. 126, 1427 (1962)
- (13) R.N. Hall and J. H. Racette, Bull. Amer. Phys. Soc. 7, 234 (1962)

- (14) K. Weiser, J. Phys. Chem. Solids 17, 149 (1960)
- (15) W.F. Schottky and M. B. Bever, Acta. Met. 6, 320 (1958)
- (16) C.D. Thurmond and M. Kowalchik, Bell Syst. Tech. J. 39, 169 (1960)
- (17) C. S. Fuller and J. M. Whelan, J. Phys. Chem. Solids 6, 173 (1958)
- (18) K. Weiser, R.S. Levitt and W.P. Dumke, to be published.
- (19) See for example L.Y. Wei, J. Phys. Chem. Solids 18, 162 (1961).

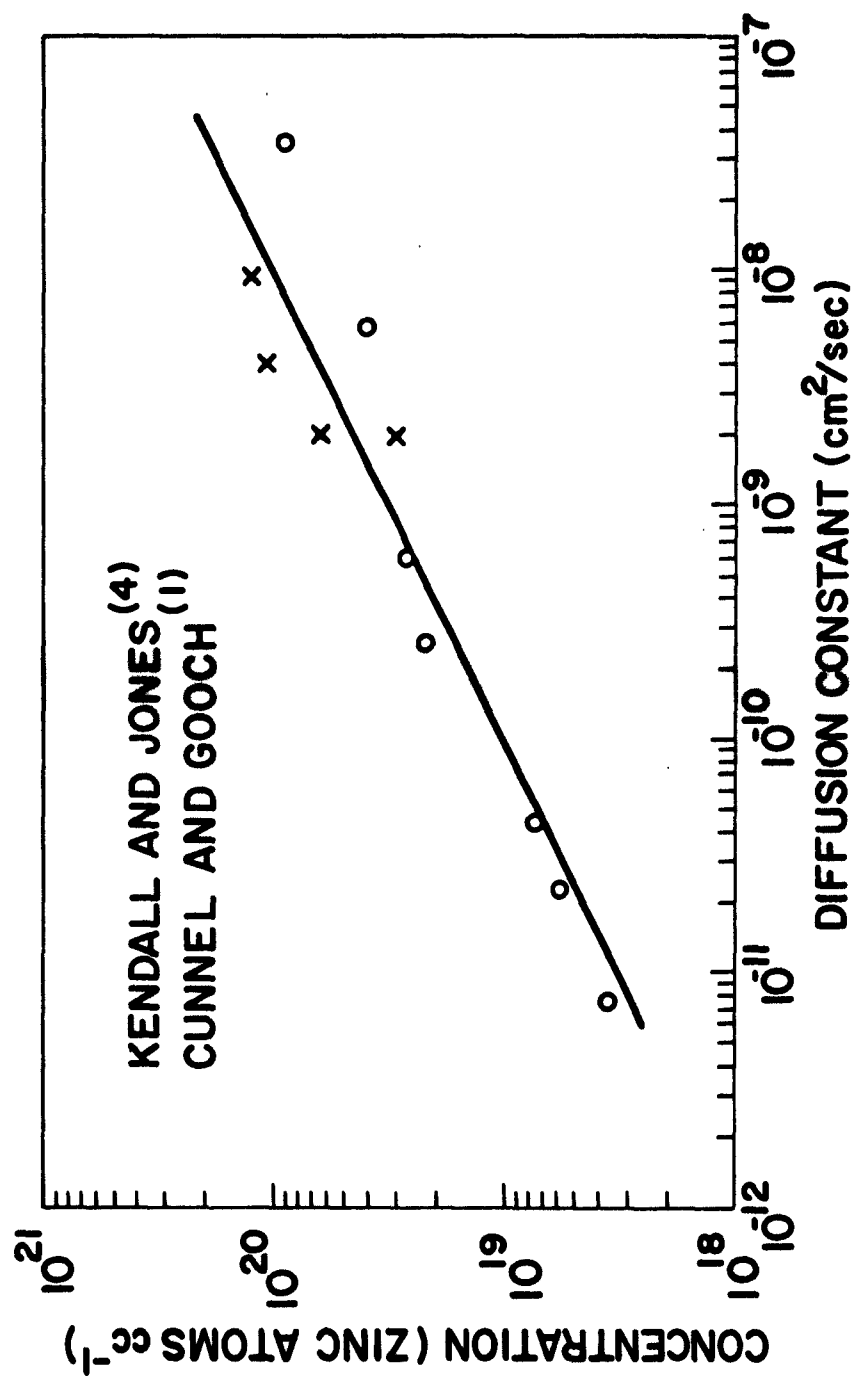


Fig. 1 Concentration dependence of the diffusion constant of Zinc in GaAs at 900°C

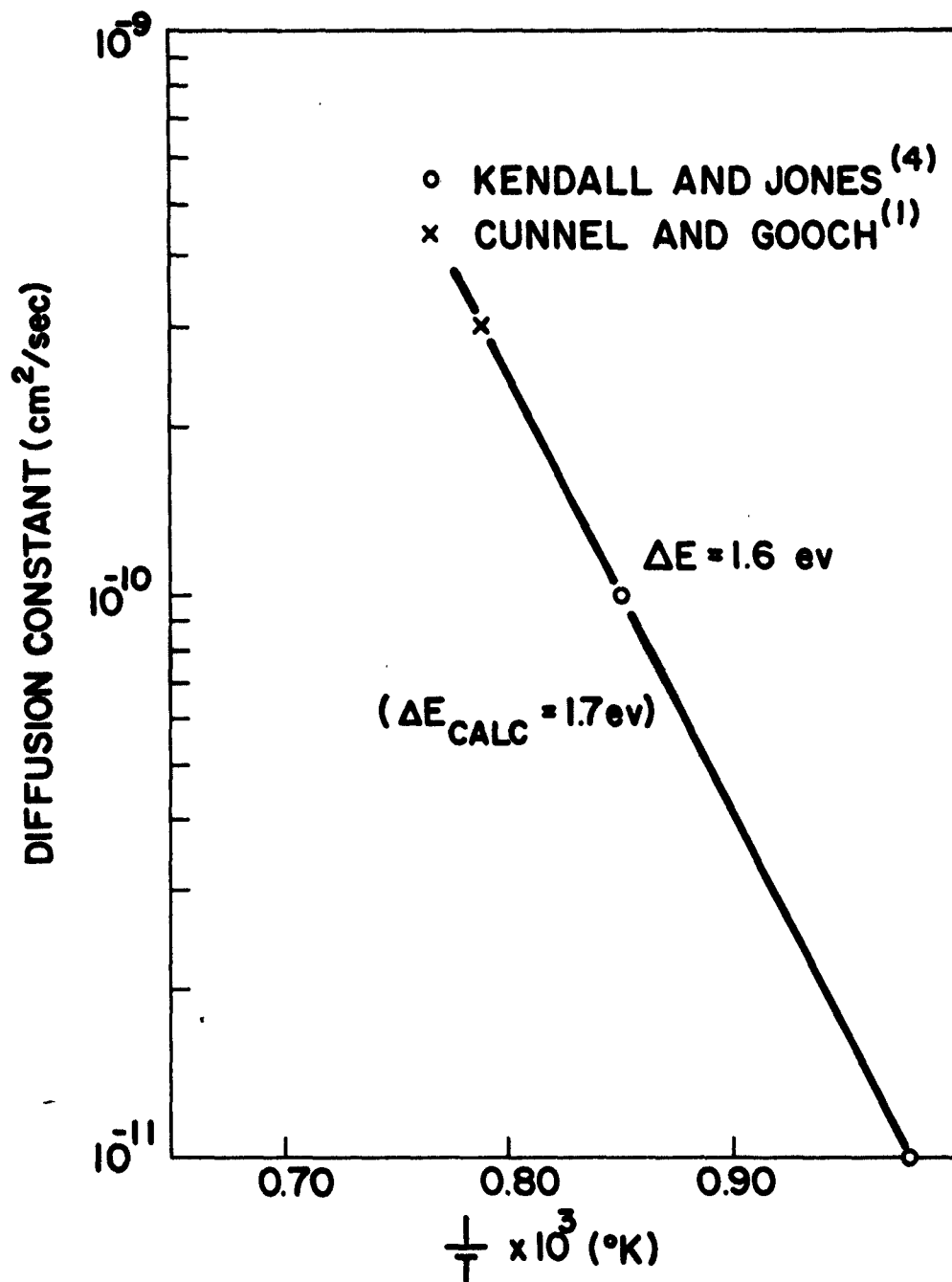


Fig. 2 Temperature dependence of the diffusion constant of Zinc in GaAs

IV. SPONTANEOUS AND STIMULATED LINE SHAPES IN SEMICONDUCTOR LASERS.

We wish to report the results of some calculations of the spectral dependence of spontaneous and stimulated emission of radiation by semiconductor injection lasers. The model used is chosen to conform to the characteristics of the recent observations of laser action in GaAs diodes. We assume that the light emission arises from electron transitions from a continuum of electron states in the conduction band to a continuum of states in the valence band. The observed spontaneous line widths at liquid helium temperatures seem to preclude the possibility that the terminal electronic states could be isolated acceptor states of definite energy. The possibility of a broadened acceptor band isolated from the valence band is not eliminated.

The crucial simplifying assumption in these calculations is that each electron has the same constant probability of recombining radiatively with each hole. We were led to this assumption by noting that the spread of crystal momenta of a hole in GaAs bound by .04 electron volts exceeds the spread of crystal momenta of conduction electrons at or below room temperature. It is certainly more accurate than the opposite assumption that electron crystal momentum is a good quantum number which is conserved in the transition.

The calculation starts by computing two spectral functions which we refer to as the spontaneous and stimulated intensity functions:

$$SP(\omega) = B \int_0^\omega d\epsilon p_-(\epsilon) p_+(\epsilon - \omega) f(\epsilon - \epsilon_-) [1 - f(\epsilon - \omega - \epsilon_+)] \quad (1)$$

$$ST(\omega) = B \int_0^\omega d\epsilon p_-(\epsilon) p_+(\epsilon - \omega) [f(\epsilon - \epsilon_-) - f(\epsilon - \omega - \epsilon_+)] \quad (2)$$

where p_- and p_+ are the densities of states in the conduction and valence bands; f is the Fermi function; ϵ_- and ϵ_+ the electron and hole quasi-Fermi levels; and B is the coefficient giving the recombination rate for unit electron and hole density.

The spectral intensity of light actually emitted from a lasing diode can be found from the number of quanta in the k^{th} electro-magnetic mode in the steady state:

$$N_k = \frac{SP(\omega_k)}{\frac{\omega}{Q_k} - ST(\omega_k)} \quad (3)$$

where ω_k is the resonant frequency of the k^{th} mode and Q_k is its quality factor.

Up to the present, calculations have been done assuming a square root dependence of both densities of states corresponding to parabolic bands. The integrals of equations (1) and (2) are done numerically by machine computation since they are not expressible in terms of tabulated functions. Figure 1 shows typical results for the spontaneous and stimulated intensity functions. If a small fraction of the electro-magnetic modes in the crystal have a high Q equation (3) predicts that the output light just above threshold is given in a typical case by Fig. 2.

34.

As the diode current is increased, in this situation, a sharp 'spike' suddenly rises out of the spontaneous line shape at a frequency very close to the maximum of the stimulated intensity function, $ST(\omega)$. Calculations are in progress using this model to predict the threshold current as a function of temperature.

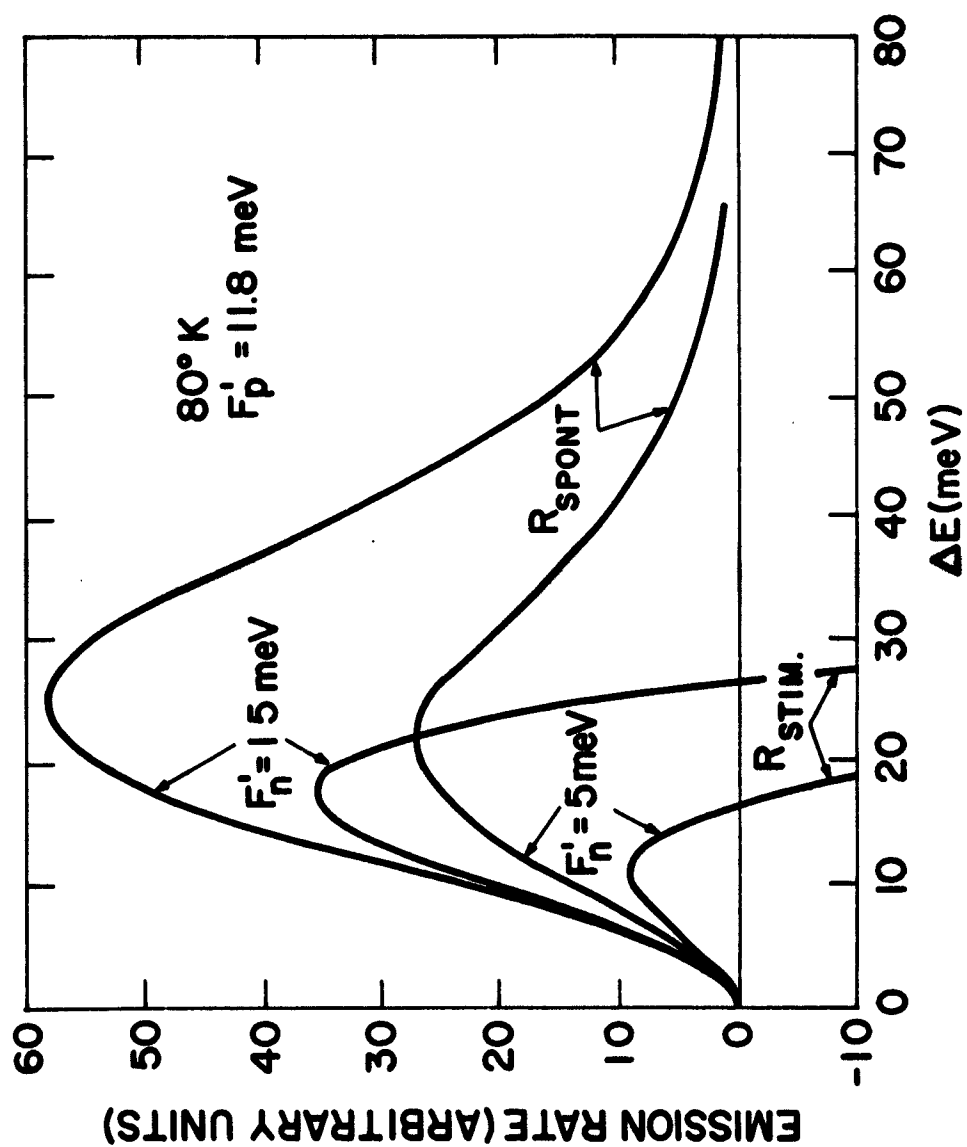


Fig. 1 Shape of the spontaneous and stimulated recombination functions

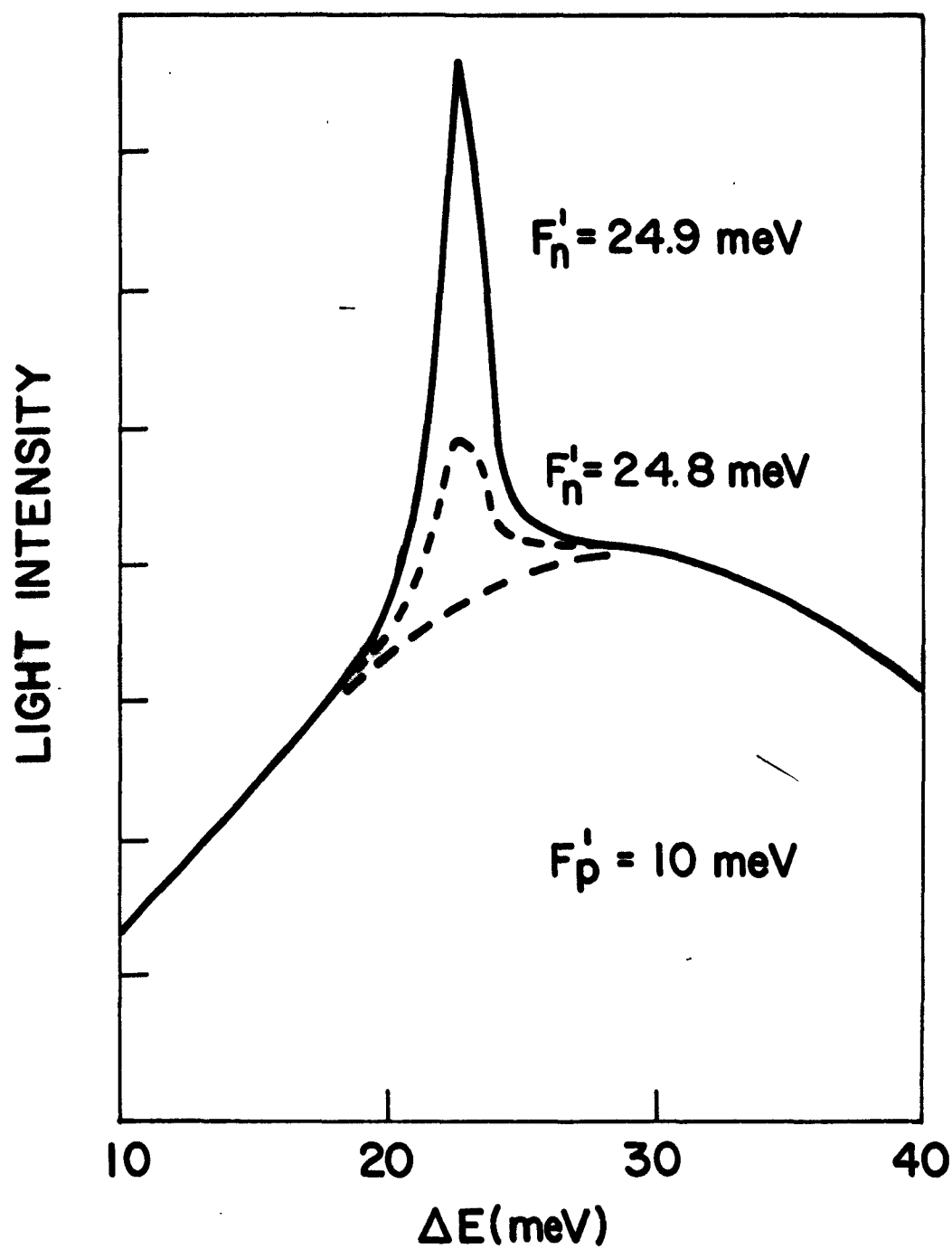


Fig. 2 Line Shape of a GaAs diode as lasing action appears

CONCLUSIONS.

The improvement in indium phosphide technology and the results of the search for stimulated emission in InP diodes have been sufficiently encouraging that further work on the subject is indicated. The InP diodes are apparently comparable to good GaAs lasers in all obviously relevant respects other than the appearance of stimulated emission.

The interpretation of the anomalous diffusion of zinc in GaAs as a mixed interstitial-substitutional diffusion is in agreement with the thermodynamic and atomistic theory of lattice defects in semiconductor crystals.

PROGRAM FOR NEXT INTERVAL.

The investigation of indium phosphide diodes will be continued. The technology of the fabrication of InP laser structures is still improving, and it is anticipated that the maximum current which can be passed through a diode will increase. The electroluminescence will be examined at 4°K , at which temperature the threshold current for onset of stimulated emission should be at least an order of magnitude smaller according to our experience with GaAs. The eventual future of the InP research will depend on the results of these experiments.

The theoretical investigation of the shapes of the emission lines will be extended to more realistic models of the band structure.

IDENTIFICATION OF KEY PERSONNEL

• R. W. Keyes - Manager, Semiconductor Physics 130 hrs.

• Dr. Keyes has been engaged in research in various aspects of solid state physics since 1950. Prior to joining IBM two years ago, he was associated with the Westinghouse Research Laboratory where he worked in high pressure physics, piezoresistance in semiconductors and thermal conductivity of solids. During 1957, Dr. Keyes served as visiting faculty member at the University of Chicago from which he received the degree of PhD. in Physics in 1953. While on the staff, he investigated the effects of hydrostatic pressure on diffusion in solids.

The activities of the Group he heads at the IBM Research Center include the study of such semiconductor phenomena as transport processes, the properties of impurity centers in crystals and the interaction of electrons with elastic waves as well as electron injection. Dr. Keyes has had a total of 32 papers published.

• G. J. Lasher - Research Staff Member. 260 hrs.

• Dr. Lasher is presently doing theoretical work in connection with the injection laser program and is also studying the temperature dependence of optical line width in ionic crystals. He was previously concerned with the effect of quantum mechanics and

irreversible statistical mechanics on computing and communication devices. One result of this work was the application of quantum principles to the channel capacity problem of information theory in order to yield a result valid at infrared and optical frequencies.

Following completion of his PhD. work at Cornell University in 1953, Dr. Lasher was a staff member of the University of California Radiation Laboratory at Livermore, California, where he engaged in theoretical investigations of nonlinear hydrodynamics. He joined IBM in 1955 and was first associated with the Applied Mathematics section of the Computing Center. Dr. Lasher later joined the Solid State Science Department where his initial work was in the field of paramagnetic resonance of defects in solids. A patent application for a microwave laser utilizing cross-saturation processes was filed on this work.

K. Weiser - Research Staff Member

520 hrs.

For several years Dr. Weiser has been actively engaged in work on impurities in semiconductors. A considerable part of his work in this field has involved the development of theories of impurity solubility and diffusion. Dr. Weiser has also had experience in materials research on III-V compounds, particularly with gallium arsenide, having spent several years on crystal growth, purification and doping and on electrical measurement of such crystals.

Until recently, Dr. Weiser's activities stressed the theoretical study of interstitial impurity diffusion and experimental work on the electrical properties of tellurium in germanium. He is now engaged in injection laser research, investigating the diffusion of transition metal, rare earth and actenide impurities in large gap semiconductors.

Dr. Weiser was awarded a Ph.D. in Physical Chemistry in 1953 by Cornell University. Prior to joining IBM in 1958, he was a member of the staff of the RCA Laboratories. His activities there included research in the preparation, evaluation and physical-chemical measurements of indium phosphide and work on the theory of distribution constants of substitutional impurities.

AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	AD- 25/4 UNCLASSIFIED 1. Luminescence 2. Optics 3. Semiconductors I. Title: Injection Lasers II. Keyes, R. W. III. Army Signal Res. & Develop. Lab., Fort Monmouth, N. J. IV. Contract DA-36-039-8C-90711 International Business Machines Corp., Research Center, Yorktown Heights, New York ELECTRON INJECTION LASER by R. W. Keyes, G. J. Lasher, E. Weiser Report No. 3 Dec. 1962-Feb. 1963 41 p. incl. illus. (Contract DA-36-039-8C-90711) Unclassified report The development of improved electron injection lasers is being pursued by attempts to fabricate lasers with new doping agents in gallium arsenide and with other semiconducting compounds. Indium phosphide technology has been developed to the point where current densities approaching 10^5 amp/cm² can be passed through electroluminescent diodes. Evidence of stimulated emission has been observed in some InP diodes at high current densities. Theoretical studies to determine the way in which various physical parameters affect the operation of an injection laser are being carried out in parallel with the experimental work.	Armed Forces Technical Information Agency UNCLASSIFIED	Armed Forces Technical Information Agency UNCLASSIFIED	Armed Forces Technical Information Agency UNCLASSIFIED	Armed Forces Technical Information Agency UNCLASSIFIED	Armed Forces Technical Information Agency UNCLASSIFIED	Armed Forces Technical Information Agency UNCLASSIFIED
---	---	---	---	---	---	---	---	---	---	---	---

AD-

UNCLASSIFIED

UNITED STATES

Injection
Lasers
Diffusion
Electroluminescence
Diffraction

AD-

UNCLASSIFIED

UNITED STATES

Injection
Lasers
Diffusion
Electroluminescence
Diffraction

AD-

UNCLASSIFIED

UNCLASSIFIED

UNITED STATES

Injection
Lasers
Diffusion
Electroluminescence
Diffraction

AD-

UNCLASSIFIED

UNCLASSIFIED

UNITED STATES

Injection
Lasers
Diffusion
Electroluminescence
Diffraction

UNCLASSIFIED

UNCLASSIFIED