Photoconductivity of Gallium Antimonide*

M. A. HABEGGER† AND H. Y. FAN
Department of Physics, Purdue University, Lafayette, Indiana
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Photoconductivity of n- and p-type GaSb has been investigated. The observed photoresponse extends beyond the threshold of intrinsic absorption. The existence of several levels in the energy gap is deduced from the spectra. With reference to the valence band, one level is located at 0.03 eV, one or two levels in the range 0.060–0.080 eV, and another level at 0.10 eV. The extrinsic photoresponse is produced by electron excitations from these levels to the conduction band. The nature of the centers which give these levels is discussed. It is deduced from the studies that n-type samples with etched surfaces have electron traps in a p-type surface layer. The level of the traps lies ≈ 0.5 eV below the conduction band, and the density of the traps is estimated to be 3×10^{12} cm^{-2}. In addition, the 0.10-eV level in the bulk material traps holes as well as giving the extrinsic photoresponse. The electron capture cross section of this level is $\approx 2\times10^{-20}$ cm^2. Electron trapping phenomena are observed in the undoped p-type material at low temperatures. Observed quenching, saturation effects, and complicated transient behavior indicate that excited states of the trap have to be taken into account. The traps have a ground-state level at 0.18 eV below the conduction band and a concentration of the order of 10^{14} cm^{-3}.

INTRODUCTION

MEASUREMENTS of photoconductivity of GaSb have been reported by Frederikse and Blunt[1] and by Lukes.[2] In these early measurements, the long-wavelength drop-off of photoconductivity was taken as indicating the energy gap, and the recombination processes were not investigated. The present study shows that the photoresponse is extended beyond the intrinsic absorption edge by the presence of levels in the energy gap. The effects of these levels have also been observed in the optical absorption and photoluminescence studies carried out concurrently in this laboratory. The positions of these levels in the energy gap are deduced from the photoconductivity spectra, and the results of the present study together with other available information provide some clue as to the nature of the centers which give rise to the levels.

The samples used in the study are obtained from single crystals grown in this laboratory. The undoped crystals are p-type with carrier concentrations $\approx 1.5\times10^{17}$ cm^{-3}. N- and p-type samples doped with Te or Se are also studied. The carrier concentrations are in the range $4\text{–}8\times10^{16}$ cm^{-3} for the compensated p-type samples and in the range $1\text{–}7\times10^{17}$ cm^{-3} for the n-type samples. Carrier-trapping phenomena are found to dominate the photoconductivity in n-type samples and in undoped p-type samples at low temperatures. The recombination processes are investigated in some detail.

The present paper relates investigations made above liquid-nitrogen temperature. Interesting oscillations in the photoconductivity spectra observed at liquid-helium temperature have been reported previously.[3] Most measurements were made with radiation chopped at a frequency of 960 cps. A phase-sensitive detection system[4] was used to measure the photoconductivity. In the cases where trapping effects produced very slow transient responses, dc coupled amplifiers and bridge circuits were used.

PHOTOCONDUCTIVITY SPECTRAL DISTRIBUTION

The measured photoconductivity will be given in terms of $\Delta G l^2/eI_0$ where ΔG is the change of sample conductance, l is the sample length, I_0 is the number of photons absorbed in the sample per unit time, and e is the electronic charge. When the change of conductivity under light excitation is small everywhere in the sample, we have

$$\Delta G l^2/I_0 e=\mu_n N_e+\mu_p N_p, \quad (1)$$

irrespective of the spatial distribution of excess carriers in the sample, provided the light-generated carriers do not reach the ends of the sample to produce contact effects. In (1), μ_n and μ_p are the mobilities of electrons and holes, and N_e and N_p are the number of excess electrons and holes in the sample resulting from the absorption of one photon per unit time. Under steady-state conditions, N_e and N_p are affected by surface recombination, and in many of our cases they are predominantly determined by trapping effects. In cases of no trapping, N_e and N_p may be regarded as the average lifetimes of electrons and holes in the sample.

The energy gap of GaSb is 0.813 eV at 4.2°K,[5] 0.80 eV at 77°K, and 0.725 eV at 300°K.[6] The photoconductivity of all GaSb samples measured above 77°K extends to

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† Present address: International Business Machines Corporation Development Laboratory, Poughkeepsie, New York.
[1] H. P. R. Frederikse and R. F. Blunt, *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), pp. 414–426.
[2] F. Lukes, Czech. J. Phys. **6**, 359 (1956).
[3] M. A. Habegger and H. Y. Fan, Phys. Rev. Letters **12**, 99 (1964).
[4] A description of the novel elements of the system will appear in Rev. Sci. Instr.
[5] S. Zwerdling, B. Lax, K. J. Button, and L. M. Roth, Phys. Chem. Solids **9**, 320 (1959).
[6] W. M. Becker, A. K. Ramdas, and H. Y. Fan, J. Appl. Phys., Suppl. **32**, 2094 (1961).

photon energies below the intrinsic threshold given by the energy gap. The extrinsic photoconductivity produced by the excitation of carriers from some level in the gap to one of the energy bands is expected to drop off at a threshold $h\nu_t$ which gives the energy separation of the level from the band. The energy separation between the level and the other band is

$$E_g - h\nu_t = \epsilon.$$

For each of the levels we are concerned with, ϵ is small and may be assumed therefore to remain unchanged while E_g and $h\nu_t$ vary with the temperature.

The drop-off in sensitivity is not sharp in the spectra measured, and the sharpness is not limited by the monochromator resolution. The values obtained for $h\nu_t$ and ϵ are therefore not precise. The four values of ϵ which are most consistent with all the photoconductivity spectra measured are (1) 0.035, (2) 0.060, (3), 0.075, and (4), 0.10 eV. Levels with approximately the same ϵ values have been deduced by Filinski[7] and Mooradian[8] from observed peaks in the photoluminescence spectra of GaSb. Arrows appropriately labeled to indicate E_g and the various $h\nu_t$'s have been placed on the measured spectra shown in Figs. 1–4. In the following discussions we shall show that all the levels are close to the valence band.

Energy Levels

The spectra of an uncompensated p-type sample are given in Fig. 1. The drop-off at low photo energies corresponds to the $h\nu_t$ of level (2) at 300 and 195°K

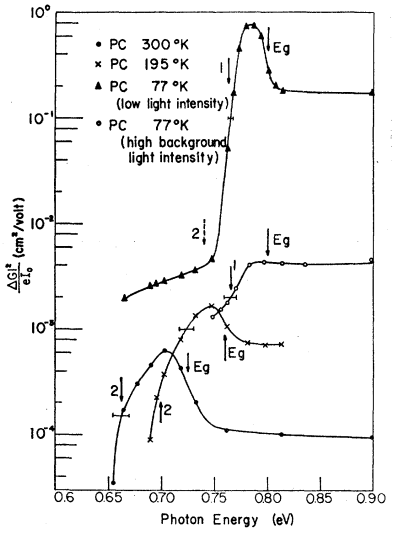

FIG. 1. Photoconductivity spectra of uncompensated p-type, GaSb sample 49A-29.

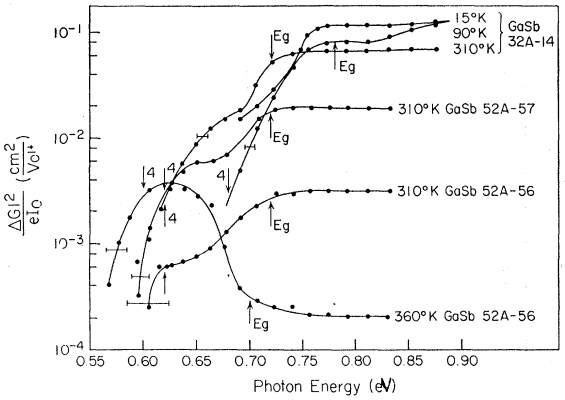

FIG. 2. Photoconductivity spectra of Te-doped, n-type, GaSb samples 32A-14, 52A-56, and 52A-57.

whereas it corresponds to the $h\nu_t$ of level (1) at 77°K. The change with temperature of ϵ indicates that level (2) is close to the valence band where the change is caused by a shift of the Fermi level from 0.07 eV at 300°K to 0.02 eV above the valence band at 77°K. At the higher temperatures, level (2), located 0.06 eV above the valence band, is sufficiently occupied to give the effect of electron excitations to the conduction band; but at the lower temperature the level is depleted of electrons. As discussed later, trapping effects are observed in the photoresponse due to level (1) in p-type uncompensated samples, showing that minority carriers or conduction electrons are generated by the excitation. This indicates that level (1) is also located near the valence band. In the vicinity of 4°K no extrinsic photoconductivity is observed because the Fermi level is too close to the valence band.

In the Te-doped n-type samples the Fermi level is located ≤ 0.07 eV from the bottom of the conduction band at all temperatures where measurements were made. As shown in Fig. 2, the drop-off of the response corresponds to the $h\nu_t$ of level (4). In these samples, level (4) with an ϵ of 0.10 eV can provide carriers by photoexcitation only if it is located near the valence band. In the Te-compensated and Se-compensated p-type samples, the Fermi level at 300°K is sufficiently high above the valence band so that a photoconductive signal due to excitations from level (4) is seen (shown in Figs. 3 and 4). Hall measurements show that the electron occupation of level (4) has decreased at 77°K. The 77°K spectra in Figs. 3 and 4 are consistent with this fact in that the response does not extend as far as is expected from level (4). The dashed low-temperature spectrum in Fig. 4 seems to contradict this expectation. Our experience has been that the compensated material is quite inhomogeneous. In spite of the fact that resistivity probing and small photovoltages indicated good homogeneity, this particular sample may have had regions where the Fermi level was considerably higher than the average estimated from the Hall coefficient.

[7] E. J. Johnson, H. Y. Fan and I. Filinski, *Preceedings of the International Conference on the Physics of Semiconductors, Exeter, July 1962* (The Institute of Physics and The Physical Society, London, 1962), p. 375.

[8] A. Mooradian (private communication).

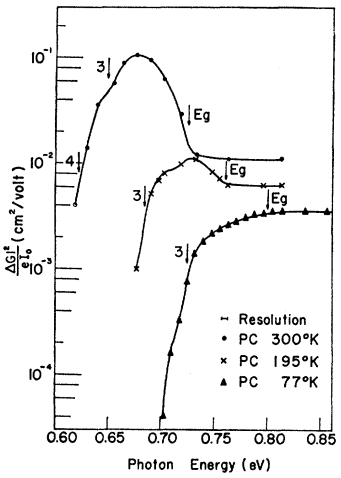

FIG. 3. Photoconductivity spectra of Se-compensated, p-type, GaSb sample 39A-32.

The 77°K spectra in Figs. 3 and 4 give the evidence for the presence of level (3) with an ϵ of about 0.075 eV. Absorption measurements of Te- and Se-compensated samples at 77°K by Johnson[9] have shown an edge in the vicinity of 17 μ. The long-wavelength absorption having the edge was attributed to excitations from the valence band to a level 0.07 eV above it. The recombination emission of these samples also showed a peak in the vicinity of 0.075 eV below the band edge. These measurements along with the photoconductivity

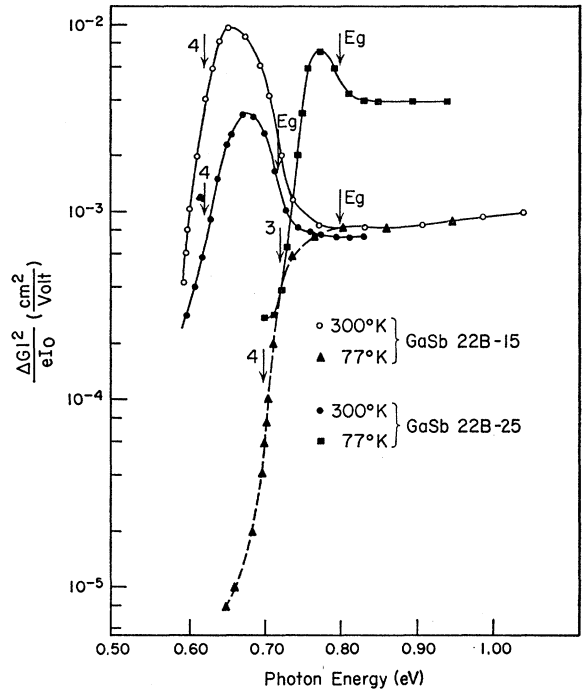

FIG. 4. Photoconductivity spectra of Te-compensated, p-type, GaSb samples 22B-25 and 22B-15.

[9] E. J. Johnson and H. Y. Fan, Sixteenth Quarterly Report of Purdue University to the U. S. Signal Corps on Semiconductor Research, 1960, pp. 11–12 (unpublished).

indicate that there is a level (3) located approximately 0.075 eV above the valence band. This level is not too far apart in energy from level (2), and it is not possible from these measurements to obtain precise values for the energy level. Therefore we can not rule out the possibility that levels (2) and (3) actually represent one level somewhere in the range from 0.060–0.075 eV from the valence band.

We consider now the possible natures of the centers which give rise to the various levels. Evidence for level (4) has been obtained only in samples which are doped with either Te or Se. No signal due to this level is observed in undoped p-type samples. This could mean either that this level is not present in the undoped

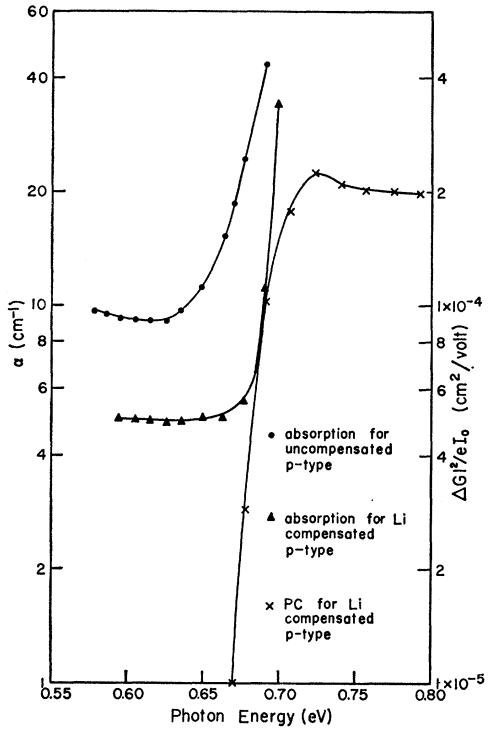

FIG. 5. Absorption and photoconductivity of a p-type lithium-doped sample at 300°K.

samples or that the Fermi level is too low for the level to be sufficiently populated. The Fermi level in undoped samples can be raised well above level (4) by lithium diffusion. The photoconductivity spectrum measured on such samples also showed no evidence of level (4). This result suggests that level (4) is introduced by Te or Se doping. Consistent with this interpretation are the recombination-emission measurements made by Filinski[7] and Mooradian.[8] A broad peak corresponding to a 0.10-eV center was observed only in p- and n-type samples doped with Te or Se. If the 0.10-eV centers were also present in the undoped p-type samples, they would have acted as radiative recombination centers for excited electrons as effec-

tively as, or possibly more effectively than, in the compensated p-type samples where the level was partially filled with electrons.

Figure 5 shows some measurements on a p-type sample into which lithium had been diffused.[10] Both the absorption and photoconductivity do not extend to as low an energy as in normal undoped samples. It appears as though the concentration of level (2) has been reduced by the lithium diffusion. Bate *et al.*,[11] on the basis of electrical measurements, have postulated that lithium forms a complex with the residual acceptor center which has two levels. The lower one of the two levels with an estimated ionization energy of 0.03 eV may be identified with our level (1). Their measurements indicate that lithium destroys level (1) and a very shallow level replaces it. Thus level (2), which according to our photoconductivity and absorption measurements is also destroyed by lithium, may be the higher level of the two-level residual acceptor center. Recombination-emission measurements by Mooradian[8] showed that the strong emission band due to level (1) became undetectable after lithium diffusion. The emission associated with level (2) was also strongly reduced. This result also suggests that levels (1) and (2) are associated with the same center.

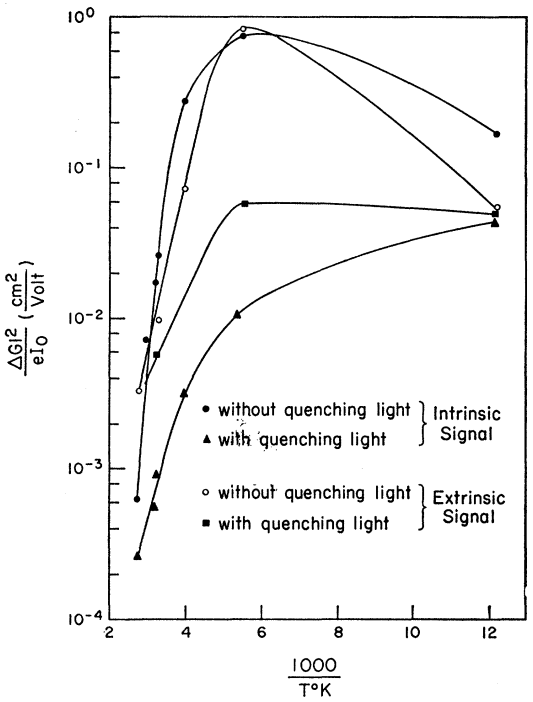

FIG. 6. Temperature dependence of the intrinsic and extrinsic quenched and unquenched photoconductive signal from the Te-doped, GaSb sample 52A-56.

TRAPPING PHENOMENA

Trapping in N-Type Samples

The magnitude of the chopped photoconductive signal of n-type samples depends quite strongly on temperature. Also, the signal can be reduced or quenched considerably by a constant background illumination from a high-intensity tungsten lamp. Figure 6 shows the temperature dependence of the intrinsic and extrinsic ac signals with and without quenching light. Figure 7 shows the quenching effect as a function of the quenching-light intensity for various temperatures. The condition where a further increase of the background-light intensity does not further appreciably reduce the ac signal is referred to as the saturation of the quenching effect.

We attribute the observed strong temperature dependence and quenching behavior to the existence of minority-carrier traps. The following observations show that the traps are located near the surface rather than distributed in the bulk. With increase of intensity of the quenching light, the ac extrinsic signal drops in a similar way and approaches the same magnitude irrespective of whether the quenching light used produces intrinsic or extrinsic excitations. Light that can produce intrinsic excitations is strongly absorbed, within $\approx 3 \times 10^{-3}$ mm of the surface, and its effect extends about a diffusion length, of the order of 0.1 mm, from the surface. On the other hand, quenching light that produces only extrinsic excitations penetrates nearly the entire thickness, ~ 1 mm, of the sample in the same way as the chopped light which produces the ac signal. If the traps are distributed in the bulk, it would be difficult to reach saturation with intrinsic quenching light as compared to the case of extrinsic quenching light. From this observation we conclude that the traps are on the surface.

It is believed that n-type GaSb has a p-type surface layer. This is indicated by the observed rectification at the metal-sample interface. According to measurements by Mead and Spitzer,[12] the Fermi level at the surface is located 0.6 eV below the conduction band. From the impurity concentration of the samples, it is estimated that the thickness of the p-type layer is of the order of 10^{-4} mm. The minority-carrier traps postulated are thus electron traps.

The surface traps are assumed to be above the Fermi level with negligible electron occupation under equilibrium conditions. In the vicinity of room temperature, the thermal excitation of the trapped electrons to the conduction band is assumed to be more probable than the recombination with holes in the valence band. As the temperature is lowered, the thermal excitation becomes more improbable and an increasing number of trapped electrons recombines by

[10] The sample was kindly supplied by R. Baxter of the Battelle Memorial Institute.

[11] R. T. Bate, R. D. Baxter, and F. J. Reid, Bull. Am. Phys. Soc. 8, 214 (1963).

[12] C. A. Mead and W. G. Spitzer, Phys. Rev. Letters **10**, 471 (1963).

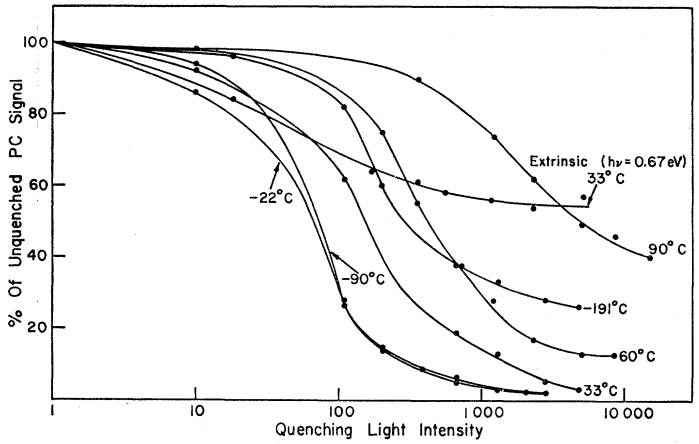

FIG. 7. The percent of the unquenched photoconductive signal as a function of the quenching light intensity. The measured curves are for different sample temperatures. The photoconductivity signal is due to chopped intrinsic light for all curves except one where chopped extrinsic light was used.

direct transition to the valence band. The ac signal measured with chopped light of low intensity may be regarded as the sum of two components

$$\Delta G=(\Delta G)_B+(\Delta G)_s.$$

The response $(\Delta G)_B$ is that of a similar crystal having no traps in the surface region. This response is assumed to be linear with light intensity; hence it is not affected by a constant background quenching light. The component $(\Delta G)_s$ represents the effect of the surface traps.

Effect of Surface Traps

The surface traps are not expected to have an appreciable effect on the rate of hole-electron recombination. Their effect on photoconductivity consists of increasing the number of free holes by a number equal to that of trapped electrons. Thus, the enhancement of the ac signal due to the traps is given by

$$(\Delta G)_s\propto A\mu_p[n_s(I_B+I_c)-n_s(I_B)], \qquad (2)$$

where n_s is the number of trapped electrons per unit surface area and is a function of I_c, the intensity of chopped light, and I_B, the intensity of background light. A is the surface area illuminated. The quenching effect comes from the decrease of $(\Delta G)_s$ with increasing I_B due to filling of the traps. The quenched curves in Fig. 6 give $(\Delta G)_B$. The difference between the quenched and unquenched curves for both intrinsic and extrinsic excitation gives $(\Delta G)_s$ for $I_B=0$.

Under steady-state conditions, the number of electrons trapped can be determined from the following equation:

$$g_{vs}(N_s-n_s)+r_{cs}n(N_s-n_s)=r_{sv}pn_s+g_{sc}n_s,$$

where n and p are the electron and hole concentrations at the surface, N_s is the surface density of traps, and the g's and r's are appropriate coefficients. The terms on the left-hand side represent the rates of electron transitions to the traps from the valence and conduction bands, respectively, and the terms on the right represent the reverse transitions. We have assumed that under equilibrium the electron population of the traps is negligible, $n_{s0}\ll N_s$, and that under light excitation $n_s\gg n_{s0}$. Furthermore, under equilibrium conditions, the transitions between the traps and the conduction band as well as the transition between the traps and the valence band must be separately balanced. Making use of these conditions, we get

$$n_s\approx N_s r_{cs}n/(r_{cs}n+r_{sv}p_0+g_{sc}). \qquad (3)$$

Since n_0 should be very small at the p-type surface, we assume n to be proportional to the light intensity I, and the proportionality will be assumed to be approximately independent of temperature. This expression in conjunction with (2) gives the dependences of $(\Delta G)_s$ on I_c and I_B.

At 227°K, the ac signal in the absence of quenching light is about 100 times larger than the signal under intense quenching light. Therefore the unquenched signal may be taken as $(\Delta G)_s$. The unquenched signal shows saturation behavior with increasing intensity I_c. The measured curve can be fitted by using (2) and (3), and the fitting yields the saturation limit of the signal. According to (3), the limit of the square bracket in (2) is N_s for large I_c and for $I_B=0$. Thus we estimate $N_s\approx 3\times 10^{12}$ cm^{-2} for the sample used.

Consider the temperature dependence of the signal. The coefficient g_{sc} for thermal excitation of electrons from the traps to the conduction band increases exponentially with temperature, depending on the activation energy E_s. From the condition that the net rate of electron transitions is zero between the traps and the conduction band, it follows

$$\frac{r_{cs}}{g_{sc}}=\frac{2}{N_c}z\exp(E_s/kT)\propto T^{-3/2}\exp(E_s/kT). \qquad (4)$$

In the absence of quenching, $I_B=0$, we get from (2) and (3)

$$(\Delta G)_s/I_c\propto\mu_p\tau_n r_{cs}/(r_{sv}p_0+g_{sc}) \qquad (5)$$

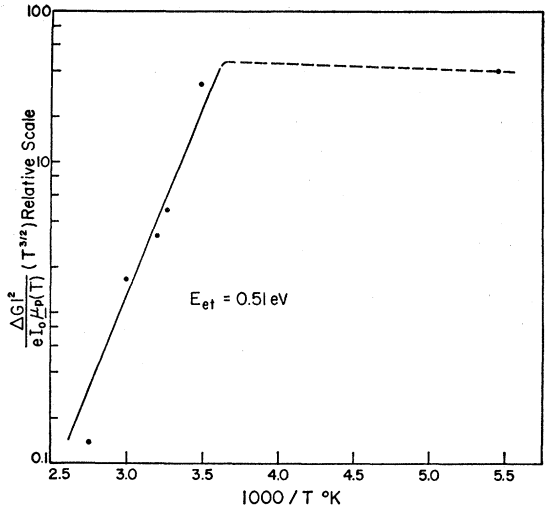

FIG. 8. The difference between the quenched and unquenched intrinsic signal multiplied by $T^{3/2}\mu_p(T)^{-1}$ plotted against reciprocal of the temperature.

for chopped light of weak intensity such that $r_{cs}n < (r_{sv}p_0+g_{sc})$. It is assumed that the electron concentration n at the surface is linear with intensity $n=\tau_n I$. At sufficiently high temperatures, we may have

$$(\Delta G)_s/I_c \propto \mu_p\tau_n(r_{cs}/g_{sc}). \tag{6}$$

In Fig. 8, the difference between unquenched and quenched signals, divided by μ_p[13] and multiplied by $T^{3/2}$, is plotted against $1/T$. Assuming τ_n is not strongly temperature dependent, the slope of the straight portion of the semilog plot gives an estimate of $E_s=0.51$ eV.

Consider now the intensity dependence of the quenching effect shown by the curves in Fig. 7. The chopped signal due to the surface traps, obtained under a background illumination I_B and chopped illumination I_c, is

$$(\Delta G)_s/I_c \propto (dn_s/dI)I_B. \tag{7}$$

From (2) and (3) we get that

$$\Delta G_s(I_B)/[\Delta G_s(0)]=[a/(I_B+a)]^2, \tag{8}$$

where

$$a\equiv(r_{sv}p_0+g_{sc})/r_{cs}\tau_n. \tag{9}$$

According to (8), $a=2.35I_B$ at

$$\Delta G_s(I_B)/[\Delta G_s(0)]=\tfrac{1}{2}. \tag{10}$$

Comparison of (6) and (9) leads us to expect a similar temperature dependence for the quantity $1/a$ and the unquenched signal. It can be seen from the curves for various temperatures in Fig. 7 that $1/a$ decreases rapidly with increasing temperature in the range above 250°K where the magnitude of the unquenched signal also decreases as shown in Fig. 6. The variation of $1/a$ in this temperature range is consistent with $E_s\approx 0.5$ eV.

We have emphasized the strong variations of the unquenched signal and the quenching effect at the high temperatures where the signal appears to be dominated by the temperature behavior of the ratio r_{cs}/g_{sc}. The fact that the variations became less steep at lower temperatures can be attributed generally to the fact that g_{sc} is no longer predominant as compared to $r_{sv}p_0$. We shall not attempt to consider in detail the temperature dependence expected from the full expression (5) or (9).

Bulk Effect

The curves of the strongly quenched signals in Fig. 6 represent the bulk effect $(\Delta G)_B$. Like the unquenched signals $(\Delta G)_s$, both curves rise steeply with decreasing temperature at the high end of the temperature range, which is suggestive of the effect of minority-carrier trapping. We assume the existence of hole traps in the bulk n-type material. Even with intrinsic excitations, the carriers diffuse to a depth of approximately 0.1 mm whereas the p-type surface layer is only of the order of 10^{-4} mm in thickness.

With intrinsic excitation, the considerations are analogous to the case of surface traps discussed above. The steep part of the intrinsic curve corresponds to an energy of 0.1–0.2 eV for the trap level above the valence band.

In the case of extrinsic excitation, conduction electrons are generated by excitations from level (4) which lies 0.1 eV above the valence band. The holes generated in level (4) may recombine directly with the conduction electrons in which case any temperature dependence of signal comes simply from the variation of the rate of this recombination. Alternatively, the holes in level (4) may take up electrons from the valence band by thermal excitation leading to the same situation as with intrinsic excitation. The second case should be more probable at higher temperature. The sharp drop indicated by the data at the high-temperature end is consistent with a trap level $E_t\approx 0.1$ eV above the valence band. Most likely the same trap level is involved in the extrinsic as well as instrinsic signals. The fact that the approximate estimates of E_t have the same order of magnitude as the ionization energy of level (4) suggests that the level itself may be the trap.

At sufficiently low temperatures, holes generated in level (4) by extrinsic excitation recombine directly with the conduction electron. This is indicated by the leveling off of the signal for $1000/T>5$. Using the lifetime τ of holes on level (4) given by the photoresponse, we can calculate the electron capture cross section σ of level (4)

$$\sigma=1/(vn_0\tau),$$

where n_0 is the equilibrium electron concentration obtained from the Hall coefficient and v is the average thermal velocity of the electrons. Thus we get $\sigma\approx 2\times 10^{-20}$ cm^2

[13] C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, Ltd., London, 1961), p. 138.

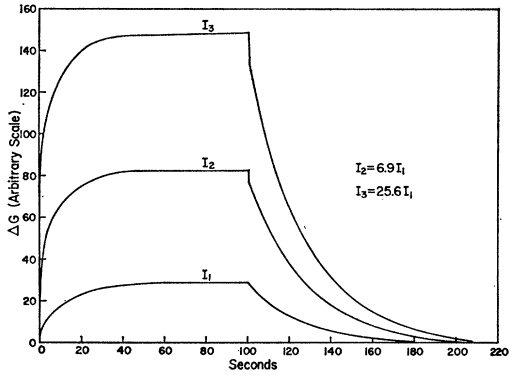

FIG. 9. The photoconductive signal of an uncompensated p-type sample at 92°K for several light intensities as a function of the time when the light was initially turned on.

Trapping in Undoped *P*-Type Samples

In undoped p-type samples, the photoresponse becomes very slow at low temperatures. Figure 9 shows the rise and the decay of the signal as a steady illumination was turned on and off. A semilog plot of the rise and the decay is given in Fig. 10 for 92°K. At the lower temperature, the decay is exponential except for a small initial drop which is found to be a bolometer effect. The drop agrees with the change of resistance calculated from the temperature change produced by illumination as measured by a thermocouple. The time constant η of the exponential decay varied strongly as shown in Fig. 11. The steady-state signal minus the bolometer effect is shown in Fig. 12 for intrinsic and extrinsic excitations. The saturation effect is clearly seen, becoming more pronounced with decreasing temperature. These phenomena are indicative of the effects of minority-carrier trapping.

The ac signal measured with chopped light at low temperatures decreases slowly with time. Such behavior is observed with intrinsic as well as with extrinsic excitation and is evidently connected with the slow rate of response. Investigation of this behavior leads to the conclusion that the phenomena observed are associated with the bulk material rather than the surface. If intrinsic excitation is used first and the signal is allowed to decay to its steady state (curve A, Fig. 13), upon changing the wavelength to the extrinsic region the signal will again show the characteristic decay from a high initial value to a steady state as shown by curve B. However, if extrinsic excitation is used first (curve C), and the wavelength is changed subsequently to the intrinsic region, the steady-state intrinsic signal is obtained immediately. We recall that the extrinsic light penetrates the entire thickness of the sample whereas the intrinsic light is absorbed in a thin layer. In the sequence A-B, only the traps near the surface are affected by the preceding intrinsic

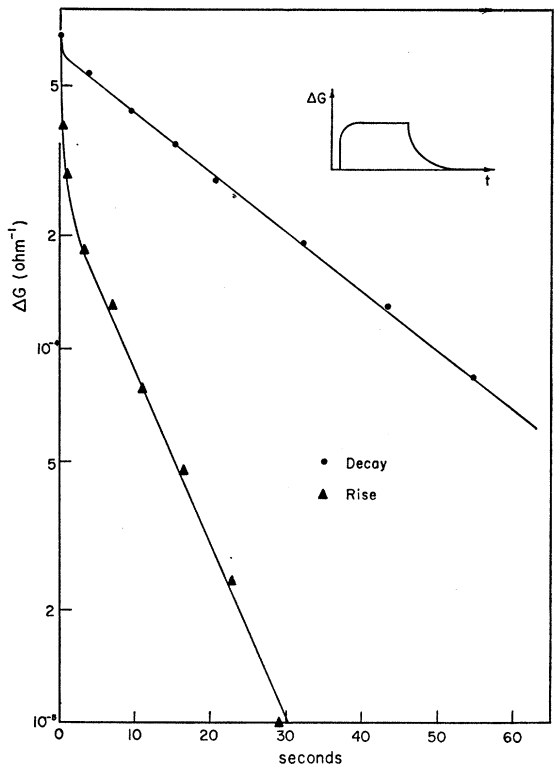

FIG. 10. A semilog plot of the rise and decay of the photoconductive signal from an uncompensated GaSb sample at 92°K.

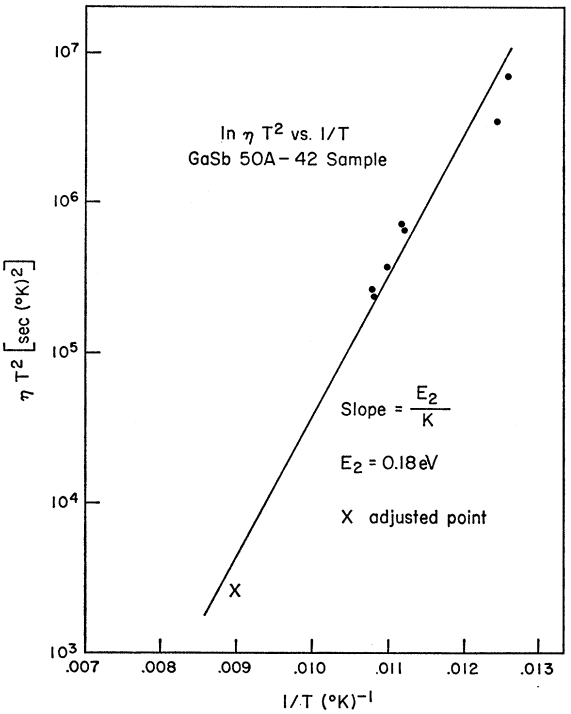

FIG. 11. Temperature dependence of the time constant for the single exponential decay of the photoconductive signal from an uncompensated p-type sample.

excitation, and the unaffected traps deep inside give the initial high signal upon changing to extrinsic excitation. On the other hand, in the sequence C-D, the traps throughout the depth of the sample are affected by the preceding extrinsic excitation and hence there is no initial high magnitude in the subsequent intrinsic signal.

The general behavior of the low-temperature photoconductivity may be ascribed to minority-carrier trapping effects. However, the usual model of a simple trapping level such as that used for the n-type samples is inadequate to account for the observed behavior. One of the complications in the present case is evident in the transient behavior. The data for 115°K show that the rise as well as the decay is not a simple exponential. They appear to have two exponential components of comparable magnitudes. Furthermore, in the temperature range 77–93°K the decay is nearly ex-

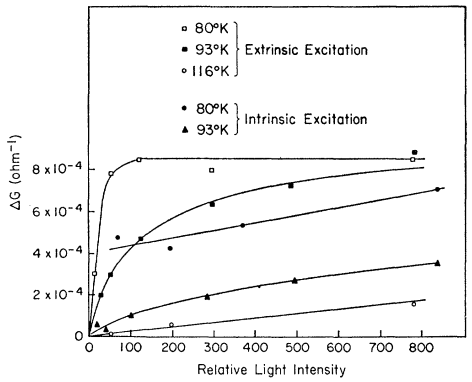

FIG. 12. The dependence on light intensity of the steady-state magnitude of the trapping photoconductive signal for intrinsic and extrinsic excitations.

ponential but not the rise, as mentioned above. This and other complications lead us to suggest that the traps have excited states with coupled differential equations of transition rates and multiple exponential transients. For simplicity we shall consider the model with one excited state shown schematically in Fig. 14. It is assumed that each center can trap no more than one electron and that direct transitions between the ground state and the conduction band can be neglected. Since the trapping is a bulk effect, we shall for simplicity deal with conductivity and carrier concentrations ignoring the effect of nonuniform excitation which is relevant for intrinsic excitation. The change of conductivity can be written

$$\Delta\sigma = e[\Delta n(\mu_n+\mu_p) - \Delta p_i\mu_p + \Delta n_t\mu_p],$$

where Δp_i is the concentration of additional holes on the impurity level which gives rise to extrinsic excitation. The expression follows from the condition of charge balance: $\Delta p = \Delta n + \Delta n_t - \Delta p_i \approx n + n_t - \Delta p_i$. The term $n_t\mu_p$ gives the effect of trapping and should be the dominant term.

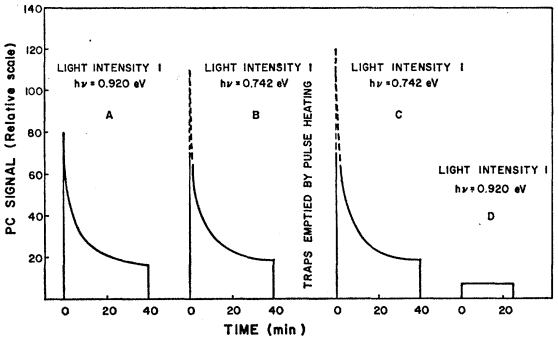

FIG. 13. The photoconductive signal as measured with the 13-cps phase-sensitive detection system plotted against the time after the light shutter was opened. The signal is from an uncompensated, p-type, GaSb sample 19B-35.

Referring to Fig. 14, we have the following equations for the electron concentrations, n_1 and n_2, in the excited and ground states of the traps:

$$\begin{aligned} dn_1/dt &= rn(N_t-n_1-n_2) - gn_1 - Rn_1 + Gn_2 \\ dn_2/dt &= Rn_1 - Gn_2, \end{aligned} \tag{11}$$

where r, g, R, and G are coefficients for the various transition rates. The measurements indicate that the lifetime of free electrons is much shorter than the transient time of the signal, and therefore we can consider that the steady-state value of n is reached immediately after a change of illumination. Also we shall take n to be proportional to the light intensity. The solution of these equations gives for n_t two exponential time-dependent terms

$$n_t = n_1+n_2 = K_+e^{-\gamma_+t} + K_-e^{-\gamma_-t} + K_0 \tag{12}$$

with

$$\gamma_\pm = B/2 \pm [(B/2)^2 - C]^{1/2}, \tag{13}$$

where

$$\begin{aligned} A &= RrnN_t, \quad B = rn+g+R+G, \\ C &= rn(R+G)+gG. \end{aligned} \tag{14}$$

Experimentally, we have in all cases one component in the transient which is much slower than the rest. In terms of the present model, this means that $\gamma_- \ll \gamma_+$. It follows that

$$\gamma_+ \approx B, \quad \gamma_- \approx C/B. \tag{15}$$

The coefficients K_+, K_-, and K_0 depend on the boundary conditions. They are different for the rise and the

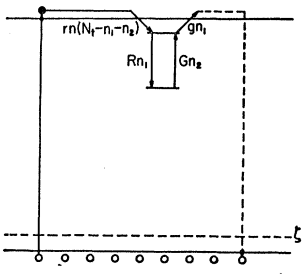

FIG. 14. Model for the trapping level with an excited state near the conduction band.

decay. However, in either case the ratio K_+/K_- is given by

$$K_+/K_-=(\gamma_-/\gamma_+)[\gamma_+-(R+G)]/[(R+G)-\gamma_-]. \quad (16)$$

It should be noted that γ_+ and γ_- may be different for the rise and decay, since rn involved in B and C is zero during the decay but not during the rise. In order to differentiate the two cases we shall use primed notations γ_+', γ_-', K_+', K_-', for the decay.

The coefficients g and G describe processes which require activation energies and should decrease with decreasing temperature while the coefficient R may be relatively insensitive to temperature. R and G are related by the relation $G=R\exp[(E_1-E_2)/kT]$. We shall now examine the experimentally observed behavior on the basis of the model. Consider first the transient decay. For the decay, $rn=0$ and (16) gives

$$K_+'/K_-'=Gg^2/\{(g+R+G)[(R+G)^2+gR]\}. \quad (17)$$

We expect that g and G become small compared to R at sufficiently low temperatures. The ratio $K_+'/K_-' \approx Gg^2/R^3$ will be very small, and only the slow component with γ_-' will be seen in the decay. Such behavior agrees with the data for $T<93$°K. At the higher temperature 115°K, the experimental data indicate two exponential components of comparable amplitudes which differ by a factor of ≈ 10 in the time constants. According to (15) and (17), $K_+'\sim K_-'$ and $\gamma_+'/\gamma_-'\approx 10$ may be obtained by having $g\geq 4R$ and $G\approx R$. The last condition requires that the energy difference between the ground and the excited state of the trap should not exceed kT corresponding to 115°K.

Consider the rise of the transient signal. Experimentally, the rise is substantially similar to the decay at 115°K. According to the model, such is the case whenever the terms with rn in B and C, (14), are unimportant. This condition is met if $rn<g$ for the intensity used in the measurement. At $T<93$°K, the rise of the observed signal differs from the decay by being much faster and by not being a simple exponential, indicating that the terms with rn are important in B and C. According to the above discussion of decay, R should be large compared to both g and G in this temperature range. From (15) we get for the transient rise

$$\gamma_+\approx rn+R, \quad \gamma_-\approx rnR/(rn+R)$$

in contrast to

$$\gamma_+'\approx R, \quad \gamma_-'\approx Gg/R \quad (18)$$

for the decay. Only the slow component γ_-' is seen in the decay. The rise will be faster than the decay, $\gamma_->\gamma_-'$ if the intensity used in the measurement gives $rn>g$. Also, we get by substituting in (16) the expressions of γ_+ and γ_-

$$K_+/K_-=(rn)^2/R(rn+R).$$

It is possible to get a large admixture of fast component, $K_+/K_-\approx 1$, with much smaller time constant, $\gamma_+\gg\gamma_-$, if rn becomes large in comparison with R. The above discussion shows that the observed transient behavior can be qualitatively accounted for by the model with

$$g\geq 4R, \quad R\gtrsim G, \quad \text{and} \quad g>rn \quad \text{at} \quad 115\text{°K}, \quad (19)$$

and

$$rn\gtrsim R>G \quad \text{for} \quad T<93\text{°K}.$$

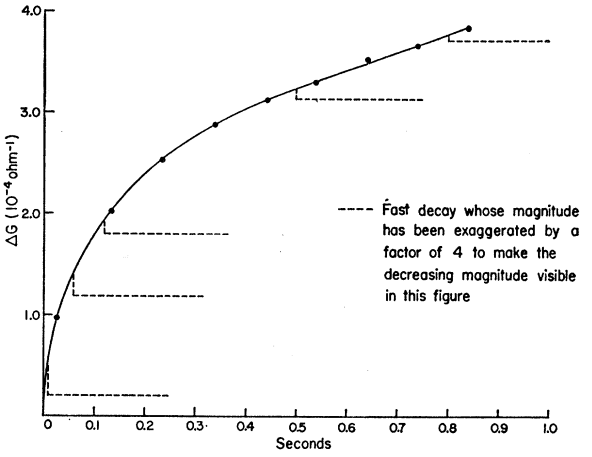

FIG. 15. The solid curve is the rise of the photoconductive signal after illuminating an uncompensated p-type sample at 92°K. The dashed line represents the rapid decay of a "fast" component followed by a slower decay rate when the illumination is suddenly turned off.

The ac response to 960 and 13 cps chopped light depends on the fast component in the decay which at low temperatures is too small to be noticeable in the complete decay curve. The decrease of ac response with time, shown in Fig. 13, comes therefore from a decrease of the fast-decay component under cumulative excitation of the light-on periods. Figure 15 shows the result of an experiment in which the fast-decay component was measured as a function of the duration t_0 of excitation. The decrease of the fast-component magnitude is clearly seen. It can be readily shown that the model gives the following dependence of K_+' (the magnitude of the fast-decay component):

$$K'\propto -\gamma_+[\gamma_-'-(\gamma_-'-\gamma_-)\exp(-\gamma_-t_0)] +\gamma_-[\gamma_-'-(\gamma_-'-\gamma_+)\exp(-\gamma_+t_0)].$$

The term $\exp(-\gamma_+t_0)$ can be neglected since t_0 used in the experiment is large compared to the time constant $1/\gamma_+$ of the fast component. Thus,

$$K_+'\propto -\gamma_-(\gamma_+-\gamma_-')\approx -\gamma_+\gamma_- \quad \text{for} \quad t_0\ll 1/\gamma_-$$

and

$$K_+'\propto -\gamma_-'(\gamma_+-\gamma_-)\approx -\gamma_+\gamma_-' \quad \text{for} \quad t_0\gg 1/\gamma_-.$$

We recall that γ_- refers to the condition under illumination and γ_-' refers to the condition without illumina-

tion. Since $\gamma_- > \gamma_-'$, the magnitude of the fast component decreases with t_0 which explains qualitatively the observed behavior shown in Fig. 15.

The ground-state energy of the trap in the model can be estimated from the temperature dependence of the slow-decay component. Under steady-state excitation, (11) gives

$$n = (Ggn_2)/\{rR[N_t - n_2(G+R)/R]\}.$$

Under thermal equilibrium

$$n_2 \ll N_t \quad \text{and} \quad n/n_2 = (N_c/2N_t)\exp(-E_2/kT),$$

where E_2 is the energy difference between the trap ground state and the conduction band. It follows that

$$Gg/(rR) = \tfrac{1}{2}N_c \exp(-E_2/kT). \tag{20}$$

For $T < 93°$K, we get according to (18)

$$\gamma_-' = Gg/R = (rN_c/2)\exp(-E_2/kT) = CT^2 \exp(-E_2/kT),$$

where r is a product of the thermal velocity and capture cross section and behaves as $T^{1/2}$ if the capture cross section is considered to be a constant over the narrow temperature interval. At 115°K, $g \gtrsim 4R$ according to (19). In this case

$$\gamma_-' = Gg/(R+g) \approx (C/5)T^2 \exp(-E_2/kT).$$

The points in Fig. 11 give $\ln(T^2/\gamma_-')$. The point marked by a cross includes the correction by a factor of 5 for the temperature 115°K. The slope of the line drawn for the best fit with the cross and the low-temperature points gives $E_t \approx 0.18$ eV. The concentration of the traps can be estimated from the saturated signal. Good saturation is observed at low temperature with extrinsic excitation as shown in Fig. 12. A concentration of $N_t \approx 10^{14}$ cm^{-3} is estimated.

The simple two-level model considered has succeeded in accounting for most of the observed unusual behaviors qualitatively, indicating that some multilevel trap is the correct picture. More detailed quantitative studies are necessary to definitely determine the model of the trap levels. It may be expected that multilevel traps are a common occurence.

CONCLUDING REMARKS

It has been mentioned in connection with (1) that an electron lifetime and a hole lifetime can be defined, $\tau_e \equiv N_e$ and $\tau_p \equiv N_p$, which determine the magnitude of response under steady-state excitation. In the absence of trapping phenomena where changes in the electron population of localized levels can be neglected, $\tau_e = \tau_p = \tau$, and the transient photoresponse is exponential with τ as its time constant. Thus the photoconductive property of the bulk material is given by a simple parameter τ, the carrier lifetime. In the presence of trapping, $\tau_e \neq \tau_p$, and the transient behavior may be quite complicated requiring detailed knowledge of the trapping processes. In n-type material, the signal, after the quenching of surface-trapping effects, is dominated by hole trapping in the bulk material. The increase of the conductance is largely due to excess electrons. From the magnitude of quenched extrinsic response, we get $\tau_e \approx 0.5$ μsec at room temperature. This quantity is determined not only by the coefficient r_{cv} of the band-to-band electron-hole recombination but depends also on the concentration and characteristics of the hole traps. In the compensated p-type samples, no obvious indications of trapping effects appeared in the measurements made in the range 300–77°K. Although strong trapping phenomena were found in undoped p-type material at low temperatures, there was no evidence of bulk trapping at room temperature. Assuming that trapping is absent, we get from the magnitudes of the steady-state signals carrier lifetimes of the order of 10 μsec for the compensated and of the order of 0.1 μsec for the undoped samples. The average carrier concentration of the compensated samples is only about four times smaller than the average carrier concentration of the undoped samples. The big ratio of the carrier lifetimes implies that the recombination coefficient, r_{cv}, of the compensated samples is smaller by at least a factor of 20.

It is interesting to compare the magnitudes of intrinsic and extrinsic responses. In all cases, the extrinsic response consists of electron excitation from a localized level to the conduction band. Such excitation in p-type samples would not be expected to give a larger response than the intrinsic response. Extrinsically excited electrons will recombine with holes in the valence band, just as in intrinsic excitation, in addition to recombining directly with the photogenerated holes in the localized levels. Extrinsic excitation is equivalent to intrinsic excitation if the photogenerated holes in localized levels capture electrons from the valence band faster than the recombinations of the excited electrons. Otherwise, the extrinsic signal should be weaker than the intrinsic signal. Experimentally, however, a higher extrinsic response is often observed as shown by the hump in some of the curves of Figs. 1, 3, and 4. We believe that this phenomenon is caused by surface recombination. Under intrinsic excitation, carriers are generated within a thin layer near the surface, and the surface recombination has a stronger effect in reducing the signal than for extrinsic excitation. The samples used had the surface etched with a mixture of nitric and hydrofluoric acids. Photoelectromagnetic measurements were made on a few samples in conjunction with photoconductivity measurements. From the combined measurements, surface-recombination velocities of the order of 5×10^4 cm/sec were obtained, large enough to account for the humps observed.