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Photocapacitance Studies of the Oxygen Donor in GaP. II. Capture Cross Sections

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Pulsed-photocapacitance measurements prove that an oxygen center in GaP can deeply capture two electrons and also provide strong evidence that this center is the isolated O donor. Measurements of the rates of capture of electrons by O and recombination rates of electrons bound to O with holes are presented. These rates were determined using a modification of the photocapacitance method. The O donor was prepared in specific charge states, in a diode depletion layer, and the changes in the trapped charge population resulting from appropriate pulsing of the diode bias voltage were then studied by photocapacitance. In this way the capture and recombination processes of interest always occurred in neutral material. The capture cross sections for electrons at 296 K were found to be $\sigma_{n1} \approx 2 \times 10^{-18}$ cm^2, $\sigma_{n2} \approx 1 \times 10^{-19}$ cm^2 for n-type material and $\sigma_{p1} \approx 4 \times 10^{-21}$ cm^2, $\sigma_{p2} > 4 \times 10^{-17}$ cm^2 for p type. (The subscripts refer to the one- and two-electron states.) The lifetimes of the bound electrons in p-type GaP with $p = (2.5 \pm 0.7) \times 10^{17}$ cm^{-3} are $\tau_{p1} \approx 46$ μsec and $\tau_{p2} < 5$ nsec. The second electron recombines with a hole without any Auger effect, since the first electron remains on the center. The transition rate is very fast and must be nonradiative. Both of these facts are consistent with the electron having a level just above the valence band, as found previously. Using σ_{n1}, a minority carrier lifetime of 13 nsec, and an O-donor density of 2.8×10^{16} cm^{-13}, the maximum O concentration reported earlier, we calculate that only about 1.5% of the recombination current is through O in p-type material.

I. INTRODUCTION

Traps in semiconductors are characterized by their concentration, energy levels, thermal-emission rates, optical cross sections, and capture cross sections. In Paper I[1] all of these properties, except the capture cross sections, were determined for the oxygen donor in GaP. In this paper we report the measurement providing three of the four capture cross sections of the O donor and indicate a lower bound for the fourth. The measurements were made by applying pulses of short duration to a diode and observing the resulting effect on the photocapacitance signals.

Photocapacitance measurements detect traps in the depletion layer of a reverse-biased junction. However, the capture cross sections of interest are actually those in a neutral material because recombination takes place primarily in the field-free region within a diffusion length of the edge of the depletion layer. The photocapacitance method can be made to provide the required information by noting that if the reverse-bias voltage of a junction is momentarily reduced, the depletion layer contracts, thereby making free carriers available for recombination processes. The time available for these processes is just equal to the time for which the bias voltage is reduced, while the spatial location in which recombination can take place is the region through which the depletion layer is moved. In this way both the temporal and spatial dependence of the processes can be investigated.

In addition, the method can be further extended to provide minority-carrier-capture rates. This is achieved by suitably forward biasing the junction, thereby injecting free carriers into the neutral material, and subsequently reverse biasing

the device to allow a photocapacitive determination of the resulting change in a trapped charge.

In our preliminary measurements of the properties of oxygen in GaP, two charge states were observed, denoted 1 and 2 for the one- and two-electron states, but it was not initially realized that these were two charge states of the same center. However, it was readily shown by pulse experiments that the recombination lifetime of state 2 was orders of magnitude shorter than that of state 1. On these grounds, one might have expected that if state 2 was suitably prepared in isolation (i.e., each center binding only one electron), a short pulse would remove the state-2 population without affecting the state-1 population. In actuality it was found that removing one electron from all the populated state-2 levels produced a new, and substantially equal, state-1 population, demonstrating that both states belong to the same center.

A very unusual property of the second electron, as discussed in Paper I, is its large increase in binding energy after capture. This remarkable behavior initially casts some doubt on the identification of the center as that of the isolated O donor. However, the fact that state 1 was found to have the same binding energy and lifetime as that of substitutional oxygen is considered strong evidence that it has been correctly identified.

Section II deals with the theory of electron capture. The experimental details are discussed in Sec. III. Section IV demonstrates that O can trap two electrons. Our measurements of the capture cross sections are reported in Sec. V. Some interpretation of these results is given in Sec. VI. The role of substitutional O as a killer center in GaP electroluminescence is discussed in Sec. VII. Finally, Sec. VIII summarizes the evidence that the center studied is substitutional oxygen, and all results are summarized in Sec. IX.

II. THEORY

In neutral material the kinetics of the O trap are governed by four capture rates c_{n1}, c_{p1}, c_{n2}, and c_{p2}, where 1 and 2 refer to the one- and two-electron states of the O center and n and p refer to the capture of electrons and holes. The capture rates are related to the capture cross sections by

$$c_{n1} = \sigma_{n1} v_n n \ , \tag{1}$$

etc., where v_n is the thermal velocity of the electrons, n is the electron density, and σ_{n1} is the cross section for capture into state 1. The populations of states 1 and 2 are coupled as shown in Fig. 1. These rates lead to two coupled equations for the densities n_1 and n_2 of two states which are formally identical to Eqs. (2) and (3) of Paper I, but with the p's and n's reversed:

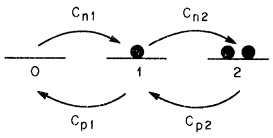

FIG. 1. Schematic diagram showing how the populations of the three charge states of O are coupled by electron and hole capture.

$$\dot{n}_1 + (c_{n1} + c_{p1} + c_{n2}) n_1 + (c_{n1} - c_{p2}) n_2 = c_{n1} N \ , \tag{2}$$

$$- c_{n2} n_1 + \dot{n}_2 + c_{p2} n_2 = 0 \ . \tag{3}$$

Consider recombination on the p side with no carrier injection. In this case, $c_{n1} = c_{n2} = 0$. The equations simplify to

$$\dot{n}_1 + c_{p1} n_1 - c_{p2} n_2 = 0 \ , \tag{4}$$

$$\dot{n}_2 + c_{p2} n_2 = 0 \ . \tag{5}$$

The capacitance transient associated with occupation of either state 1 or state 2 will be the sum of two exponentials with time constants

$$\tau_{p2}^{-1} = c_{p2} = \sigma_{p2} v_p p \ , \tag{6}$$

$$\tau_{p1}^{-1} = c_{p1} = \sigma_{p1} v_p p \ . \tag{7}$$

It is obvious from Fig. 1 that the steady-state values of n_1 and n_2 are zero.

For capture of electrons on the n side, in the absence of hole injection, c_{p1} and c_{p2} are zero and the rate equations become

$$\dot{n}_1 + (c_{n1} + c_{n2}) n_1 + c_{n1} n_2 = c_{n1} N \ , \tag{8}$$

$$- c n_2 n_1 + \dot{n}_2 = 0 \ . \tag{9}$$

The steady-state values of n_1 and n_2 are $n_1 = 0$ and $n_2 = N$, as expected from Fig. 1. Once more the transient is the sum of two exponentials with time constants

$$\tau_{n1}^{-1} = c_{n\,1} = \sigma_{n1} v_n n \ , \tag{10}$$

$$\tau_{n2}^{-1} = c_{n2} = \sigma_{n2} v_n n \ . \tag{11}$$

Thus the capture cross sections can be measured directly from the decay rates.

If the diode is in forward bias, all the rates are nonzero. The steady-state values of n_1 and n_2 are given by

$$n_1 = \left[1 \Big/ \left(1 + \frac{c_{p1}}{c_{n1}} + \frac{c_{n2}}{c_{p2}} \right) \right] N \ , \tag{12}$$

$$n_2 = \left[\frac{c_{n2}}{c_{p2}} \Big/ \left(1 + \frac{c_{p1}}{c_{n1}} + \frac{c_{n2}}{c_{p2}} \right) \right] N \ . \tag{13}$$

The transient time constants are the roots of the secular equation

$$\lambda^2 - (c_{n1} + c_{p1} + c_{n2} + c_{p2}) \lambda + c_{p2}(c_{n1} + c_{p1}) + c_{n2} c_{n1} = 0 \ . \tag{14}$$

In our studies, in electron injection into the p side the fastest rate by far is c_{p2}. In this case Eq. (14)

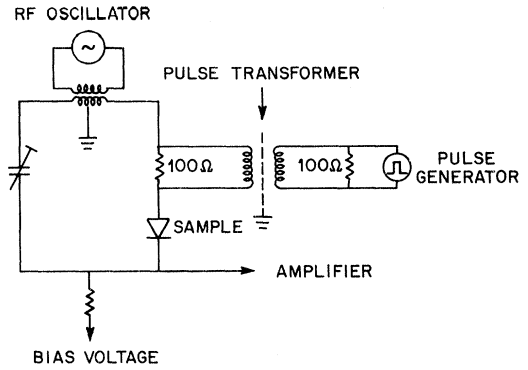

FIG. 2. Schematic diagram of the bridge of a Boonton model 71A capacitance meter modified with a pulse transformer.

simplifies to

$$\lambda^2 - c_{p2}\lambda + c_{p2}(c_{n1}+c_{p1}) = 0 \ . \tag{15}$$

From the roots of this equation we see that the slower time constant, corresponding to the occupation of state 1, is given approximately by

$$1/\tau \approx c_{p1}+c_{n1} = 1/\tau_{p1}+\sigma_{n1}v_n n \ . \tag{16}$$

III. EXPERIMENTAL METHOD

The experimental equipment used was that described in Paper I, with the addition of a Systron-Donner 110-B pulse generator with transformers for proper impedance match. A pulse up to 10-V amplitude of either polarity could be added to the diode bias. A simplified schematic is shown in Fig. 2. Two different transformers were required to cover the pulse-duration range of 20 nsec to 5 μsec. By recording ΔC as a function of the number of pulses, various rates were measured. This is equivalent to measuring ΔC versus pulse duration.

IV. EVIDENCE THAT STATES 1 AND 2 BELONG TO SAME CENTER

The capacitance changes, demonstrating that states 1 and 2 belong to the same center, are shown in Fig. 3(a). Initial irradiation with visible light partially filled states 1 and 2, thereby increasing the diode capacity. As shown in Paper I, O is mainly in p-type material in this diode, hence, filling O states with electrons increases capacity. A slight decrease in capacitance when the visible light was blocked was primarily caused by the edge effects discussed in Sec. III C of Paper I. Electrons in state 1 were then completely removed by 1-eV ir radiation which results in capacitance change $\Delta C_{ir}^{(1)}$. A 50-nsec-duration pulse of about 8 V was then applied to the diode which reduced the 9-V bias to 1 V. The duration of this pulse was long enough to completely empty state 2, but too short to affect state 1. This causes an abrupt decrease in junction capacitance shown as ΔC_{pulse} in Fig. 3(a). The surprising fact was that after the pulse, electrons were again observed in state 1. This was shown by a second ir irradiation which emptied state 1 only, producing an additional decrease in capacitance $\Delta C_{ir}^{(2)}$.

In Fig. 3(b), again states 1 and 2 are partially filled optically, but first the pulse was applied and then the junction was irradiated with ir light. The capacitance decrease during the pulse is the same as in Fig. 3(a):

$$\Delta C_{pulse} = \Delta C'_{pulse} \ , \tag{17}$$

and the capacitance decrease due to ir light is the same as the total change in Fig. 3(a):

$$\Delta C'_{ir} = \Delta C_{ir}^{(1)} + \Delta C_{ir}^{(2)} \ . \tag{18}$$

The capacitance changes $\Delta C_{ir}^{(1)}$ and $\Delta C_{ir}^{(2)}$ are identified as being due to the same state since they have the same exponential decay rates, as shown in Fig. 4. Here the various capacitance changes $\Delta C_{ir}^{(1)}$, $\Delta C_{ir}^{(2)}$, and $\Delta C'_{ir}$ are shown to have the same time decay rate at three different ir energies. This proves that the ir light removes electrons only from state 1.

The simplest explanation of these experiments is to assume that states 1 and 2 are different charge states of the O center. Since state 1 corresponds to the addition of a single electron to the O donor,

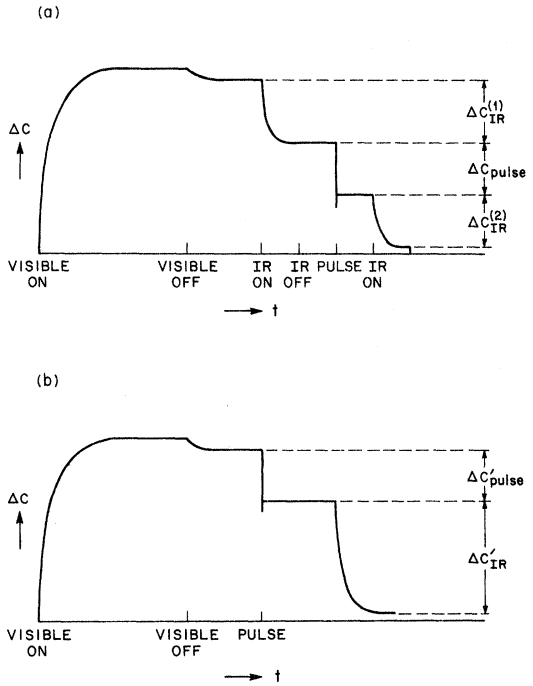

FIG. 3. Capacitance changes showing that the pulse removes an electron from state 2 and adds another electron to state 1.

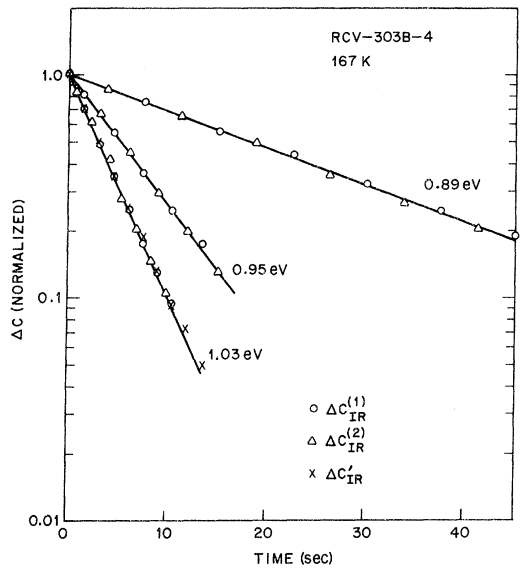

FIG. 4. Decay rates $\Delta C_{ir}^{(1)}$, $\Delta C_{ir}^{(2)}$, and $\Delta C_{ir}'$. The three capacitance changes decay at the same rate at each ir energy and must be associated with the same state.

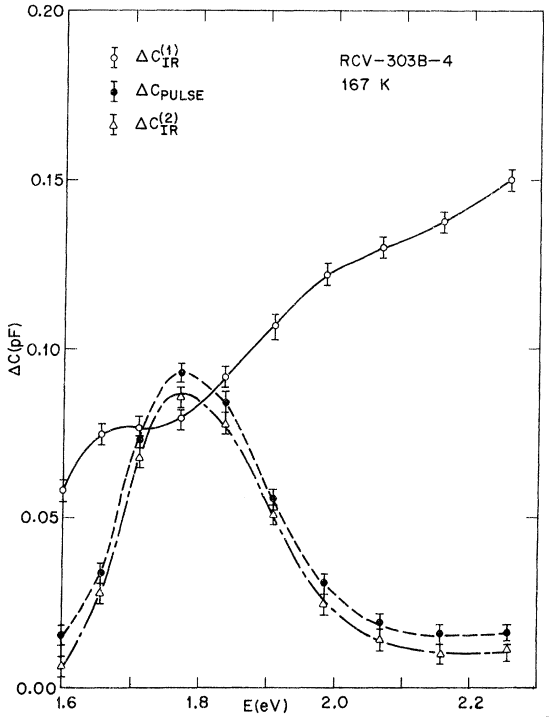

FIG. 5. Capacitance changes $\Delta C_{ir}^{(1)}$, $\Delta C_{ir}^{(2)}$, and $\Delta C_{pulse}'$ for initial states prepared with irradiation of visible light of energy E. The data show that $\Delta C_{ir}^{(2)} \approx \Delta C_{pulse}$.

state 2 must correspond to O gaining a second electron. Now referring to Fig. 3(a) again, the visible light partially fills each state causing increased capacitance. That is, some O centers have two electrons, some have one electron, and some have no electrons. (The centers with no electrons produce no capacitance change.) The ir light removes electrons from the O donors with one electron, causing decrease $\Delta C_{ir}^{(1)}$. The pulse removes one electron from the O donor in state 2, changing those donors from state 2 to state 1 and causing capacitance decrease ΔC_{pulse}. The electrons in state 1 are then removed with the second ir light irradiation, resulting in the decrease $\Delta C_{ir}^{(2)}$.

This model predicts that

$$\Delta C_{ir}^{(2)} = \Delta C_{pulse} . \tag{19}$$

This was experimentally confirmed by the results shown in Fig. 5. The amplitude of ΔC_{pulse} is proportional to the occupation of state 2, which is a function of the visible-light energy. The quantities ΔC_{pulse}, $\Delta C_{ir}^{(2)}$, and $\Delta C_{ir}^{(1)}$ versus photon energy show a large variation in ΔC_{pulse} and that $\Delta C_{ir}^{(2)} \approx \Delta C_{pulse}$ over the entire range.

V. MEASUREMENT OF CAPTURE RATES

A. Hole-Capture Rates in p-Type Material

The hole-capture rates were measured at 296 K. Initially, the diode was irradiated with visible light which partially populated states 1 and 2 and caused capacitance changes ΔC_1 and ΔC_2. During the pulse the diode bias of 10 V was reduced to 1 V. The rates τ_{p1}^{-1} and τ_{p2}^{-1} were measured by observing the decrease in ΔC_1 and ΔC_2 with the number of short pulses applied to the diode. The nar-

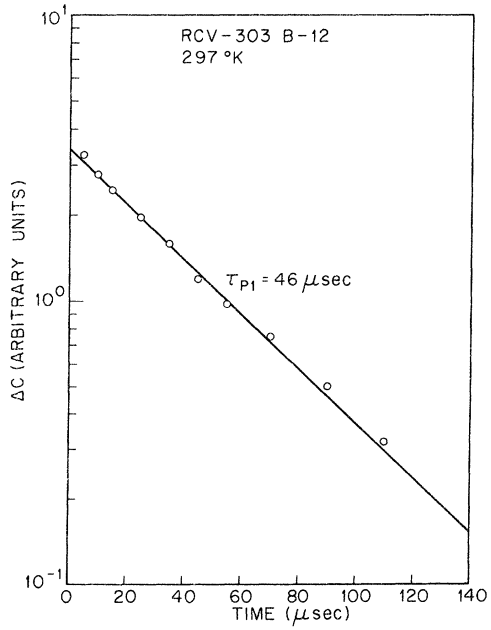

FIG. 6. Decay of ΔC_1 vs time. The time is equal to the total duration of the 5-μsec pulses applied to the diode junction.

rowest pulse we could apply was 20 nsec in duration. This pulse completely removed all electrons in state 2 proving that $\tau_{p2} < 5$ nsec. This was also true at 167 K. The decay of state 1 shown in Fig. 6 is the measured capacitance change plotted against cumulative pulse on time applying 5-μsec pulses. These data give $\tau_{p1} \approx 46 \pm 5$ μsec at 296 K.

The sample has $N_A - N_D \approx 4.2 \times 10^{17}$ cm^3. Comparisons of Hall and capacitance determinations of carrier concentrations in p-type GaP show that room-temperature hole concentrations are usually 1.5–2.0 times less than $N_A - N_D$.[2] If we estimate $p = (2.5 \pm 0.7) \times 10^{17}$ cm^{-3} and the thermal velocity to be $v_p = 2 \times 10^7$ cm/sec, then the hole-capture cross sections given by Eqs. (6) and (7) are

$$\sigma_{p1} = (4.4 \pm 1) \times 10^{-21} \text{ cm}^2 , \quad \sigma_{p2} > 4 \times 10^{-17} \text{ cm}^2 .$$

B. Electron Capture in p-Type Material

We can measure the electron-capture cross sections on the p side by observing the occupation of the O states when carriers are injected. Unfortunately, τ_{p2} is quite short, which makes this state very difficult to saturate. We were unable to observe any occupation of this state with diode currents up to 50 mA (36 A/cm^2). On the other hand, state 1 can readily be saturated at currents of a few mA. It was shown in Sec. II that the population of this state will increase to a stationary value at rate

$$\tau^{-1} = \tau_{p1}^{-1} + \sigma_{n1} v_n n . \tag{16}$$

This rate was measured by pulsing the diode to forward bias, partially filling state 1. After the pulse, the junction capacitance increased by ΔC_1. The change in capacitance approached a steady

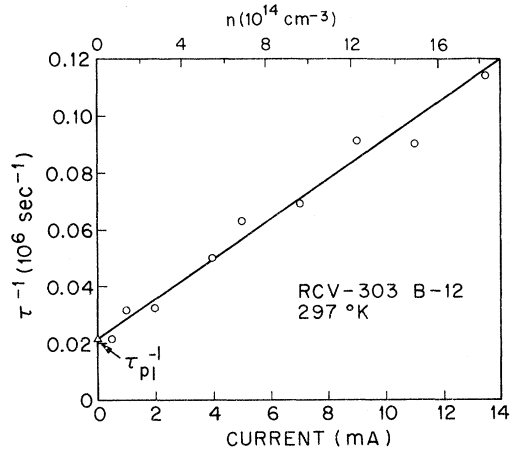

FIG. 7. τ^{-1}, the rate at which state 1 approaches its steady-state value, vs junction current (lower scale) and estimated injected carrier concentration (upper scale). The triangular point at zero current is τ_{p1}^{-1} measured in Fig. 6.

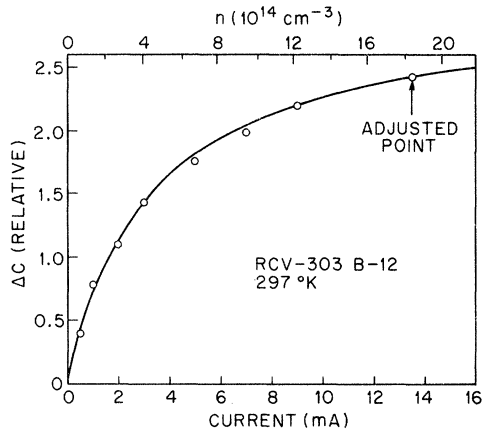

FIG. 8. Steady-state capacitance change ΔC_1 vs junction current (lower scale) and estimated injected carrier concentration (upper scale). The solid curve is given by Eq. (22). The one adjusted parameter is $\Delta C_{1\,\max}$ fitted with the data point at 13.5 mA.

state after a series of 1-μsec pulses. Rate τ^{-1} is plotted as a function of the injected carrier concentration n in Fig. 7. The intercept at $n = 0$ gives τ_{p1}. This value is in excellent agreement with our previous determination of τ_{p1} shown by the triangular data point. Taking v_n to be 2×10^7 cm/sec, we determine σ_{n1} from the slope of the data points to be

$$\sigma_{n1} = (2.6 \pm 1.0) \times 10^{-18} \text{ cm}^2 .$$

The uncertainties arise from the difficulty of estimating n, where n is related to the current I through the diode by

$$n = (\gamma L_n / qAD_n) I , \tag{20}$$

where γ is the injection efficiency, D_n is the electron-diffusion coefficient, and L_n is the diffusion length $[= (D_n \tau_n)^{1/2}]$. If we take $D_n = 2.5$ cm^2 sec^{-1}, $A = 1.45 \times 10^{-3}$ cm^{-3}, and estimate $\gamma \approx 0.5$ and the minority carrier lifetime τ_n as 10 nsec, evaluation of Eq. (20) gives

$$n = (1.4 \pm 0.6) \times 10^{14} I(\text{mA}) \text{ cm}^{-3} . \tag{21}$$

The data in Fig. 7 cover a current range from 0.5 to 13.5 mA. Additional data up to 40 mA gave the same value for σ_{n1}.

The saturation of state 1, as the injected carrier concentration is increased, is given by Eq. (12). Since we were unable to observe any injected occupation of state 2, we may neglect the term c_{n2}/c_{p2}. We can then rewrite Eq. (12) as

$$\frac{\Delta C_1}{\Delta C_{1\,\max}} = \frac{n_1}{N} = \frac{\sigma_{n1} v_n \tau_{p1} n}{1 + \sigma_{n1} v_n \tau_{p1} n} . \tag{22}$$

The saturation data are shown in Fig. 8. The solid curve is a theoretical fit using capture rate $\sigma_{n1} v_n n$, determined from the slope of Fig. 7 and

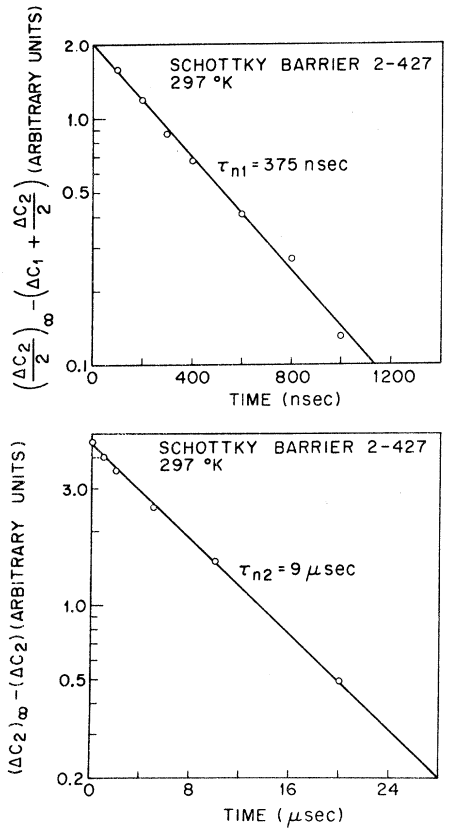

FIG. 9. (a) Exponential increase of $\Delta C_1 + \frac{1}{2}\Delta C_2$ to its final value $\frac{1}{2}(\Delta C_2)_\infty$. (b) Exponential increase ΔC_2 to its final value $(\Delta C_2)_\infty$.

$\tau_{p1} = 46$ μsec, determined from the data in Fig. 6. The one unknown parameter $\Delta C_{1\,\max}$ was adjusted to fit the data at $I = 13.5$ mA. The agreement between theory and experiment is excellent.

The linear relation of τ^{-1} with I, as well as the simple saturation behavior of ΔC_1 vs I, implies that the proportionality of n and I, given by Eq. (21), must hold over the entire current range from 0.5 to 40 mA. Apparently space-charge recombination, which tends to reduce n, is negligible at currents of 0.5 mA or higher.

C. Electron Capture in n-Type Material

The rates of capture of electrons in states 1 and 2 were conveniently measured with a Schottky barrier on n-type O-doped GaP. The sample was biased at -8 V. States 1 and 2 were emptied by irradiating the sample with 1.5-eV light and then by 1-eV light. The diode was then pulsed to a bias of -4 V, swithching the centers of interest from the depletion layer to n-type material and partially filling states 1 and 2.

After one or more pulses, the diode capacitance is changed by $\Delta C_1 + \Delta C_2$, where $\Delta C_1 \propto n_1$ and $\Delta C_2 \propto 2n_2$. The diode was then irradiated with 1-eV light, removing change ΔC_1, and 1.5 eV, followed by 1-eV light, removing change ΔC_2. This procedure allowed us to measure ΔC_1 and ΔC_2 as a function of the number of pulses applied to the diode. ΔC_1 increased at first as state 1 became occupied and then decreased as a second electron was captured and state 1 was converted to state 2. After many pulses all of the O donors were in state 2. The capacitance change was $(\Delta C_2)_\infty$.

The changes ΔC_1 and ΔC_2 are governed by Eqs. (8) and (9). These equations are coupled. If we add Eqs. (8) and (9), we get a single equation for $n_1 + n_2$:

$$\frac{d}{dt}(n_1+n_2) + c_{n1}(n_1+n_2) = c_{n1}N \,. \tag{23}$$

The capacitance change proportional to n_1+n_2 is $\Delta C_1 + \frac{1}{2}\Delta C_2$. This combination of the capacitance changes will exponentially approach the stationary value $\frac{1}{2}(\Delta C_2)_\infty$ at rate $c_{n1} = \tau_{n1}^{-1}$ as shown in Fig. 9(a).

We found $\tau_{n2} = c_{n2}^{-1}$ to be about 20 times longer than $\tau_{n1} = c_{n1}^{-1}$, so that at long times ΔC_2 increases exponentially with rate c_{n2} to a final value of $(\Delta C_2)_\infty$. The measured changes are shown in Fig. 9(b). Averages over several measurements gave $\tau_{n1} = 0.45 \pm 0.1$ μsec and $\tau_{n2} = 8 \pm 1$ μsec. We estimate the carrier concentration in the sample to be $n \approx 6\times10^{16}/\text{cm}^3$ and $v_n = 2\times10^7$ cm/sec^{-1}. This leads to

$$\sigma_{n1} \approx 2\times10^{-18}\ \text{cm}^2\,, \qquad \sigma_{n2} \approx 1\times10^{-19}\ \text{cm}^2$$

at 296 K. The value of σ_{n1} is in good agreement with the value of this cross section measured by electron injection.

The temperature dependence of σ_{n1} and σ_{n2} is shown in Fig. 10. These data were taken on a p^+n junction lightly doped with O and are not as accurate as the room-temperature values quoted above.

VI. COMMENTS ON RECOMBINATION MECHANISMS

A. Hole Recombination into State 2

The experiments described in Sec. IV show that when the O donor is in state 2, electron-hole recombination removes only one of the two electrons, leaving the center in state 1. This means that the Auger effect, in which one of the electrons recombines with a hole and the other electron is ionized, does not take place. This may seem surprising since this is the dominant recombination mechanism for bound excitons (two bound electrons and a bound hole) in GaP.[3] Dean *et al.*[4] in a study of excitons bound to acceptors in GaP showed that the Auger recombination rate increases rapidly with binding energy. The increase in Auger recombination with binding energy is also expected for donors. Therefore one might expect the Auger

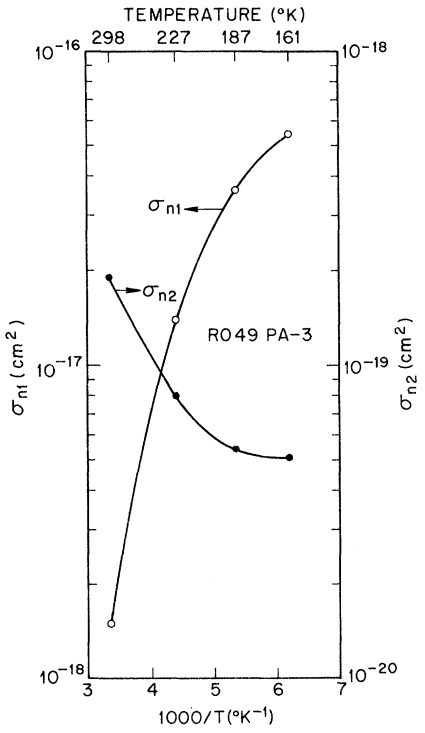

FIG. 10. σ_{n1} and σ_{n2} vs temperature.

effect to dominate the hole recombination of state 2. In the case of O, however, the binding energy is so great that the Auger effect is energetically not possible. The binding energy depends upon the lattice coordinates as discussed in Sec. III B of Paper I. On the average, the optical-ionization energy of an electron in state 2 is 2 eV. Thus the average energy gained in recombination with a hole is only about 0.3 eV, not nearly enough to ionize the other electron. The short decay time τ_{p2} (less than 5 nsec) indicates that the recombination is nonradiative. Presumably this energy is dissipated by phonon emission.

The studies in Paper I show that the second electron is captured in a state that is ≈ 0.45 eV below the conduction band before lattice relaxation. It is possible that Auger recombination could occur before the lattice has a chance to relax. If this effect were significant, the saturated value of n_1 would be much less than N. We have measured n_1/N at saturation and have found that it is equal to unity within an error of $\pm 20\%$. Thus all Auger effects associated with the two-electron state of O seem to be negligible.

B. Electron Capture into State 1

The temperature dependence of electron capture into state 1 was measured in lightly doped n-type material. The capture cross section was found to decrease by a factor of 30 when the temperature was increased from 131 to 296 K. Dean and Henry[5] studied luminescence associated with capture into state 1 at helium temperature. They found that the electron is captured into a shallow level ≈ 0.06 eV below the conduction band and then radiatively decays to the ground state.

If the electron is captured into a shallow level, thermalization out of this level will cause the cross section to rapidly decrease with increasing temperature, as observed.

Jayson *et al.*[6] have observed an unusual sublinear saturation behavior of the ir luminescence in Zn- and O-doped GaP. They interpreted their data in terms of a model in which O captures a second electron and undergoes Auger transitions, which prevent the one-electron state of O from saturating. Analysis with this model led them to conclude that the capture cross section into the one-electron state is about 2×10^{-17} cm^2 in a sample with $p\approx 2\times10^{+17}$ cm^2.

In contrast to their results, we observed a simple saturation of state 1 (see Fig. 8) of O with a capture cross section of about 2×10^{-18} cm^2. It is interesting that in Cd- and O-doped GaP and in C- and O-doped GaP, Jayson *et al.*[6] did not observe unusual saturation behavior of the ir luminescence. It may be that in their Zn-doped crystals, another transition with different saturation properties is contributing the to ir luminescence.

C. Electron Capture into State 2

The second electron is captured by a neutral center which is not expected to have any shallow states. In this case we do not expect the capture cross section to vary appreciably with temperature. However, the cross section is found to slowly increase with temperature. This is not yet understood.

VII. ROLE OF O AS KILLER CENTER

The amount of recombination through the O center is specified by the O concentration, capture cross sections, and the minority-carrier lifetime. In the absence of saturation, recombination in p-type material takes place only through state 1. The volume-recombination rate through O is given by $N\sigma_{n1}v_n n$. The total volume-recombination rate is $n\tau_n^{-1}$, where τ_n is the minority-carrier lifetime in p-type material. Therefore, the fraction of the recombination current through the O center f_0 is

$$f_0 = N\sigma_{n1}v_n\tau_n \,. \tag{24}$$

Jayson *et al.*[6] measured the minority-carrier lifetimes of a variety of Zn- and O-doped GaP samples. The highest value they report is 13 nsec. If we take $N=2.8\times10^{16}$/cm^3 (the highest value reported in Paper I), $\sigma_{n1}=2\times10^{-18}$ cm^2, $v_n=2\times10^7$ cm/sec, and $\tau_n=13$ nsec, we find

$f_0 = 0.015$.

Using the same minority-carrier lifetime, Jayson *et al.*[6] estimate that the fraction of recombination through the O center is 0.33. This large value was arrived at by using a larger concentration (7×10^{16} cm^{-3}) and a much larger capture cross section ($\sigma_{n1}\approx 2\times10^{-17}$ cm^2) than we have observed.

As state 1 of O becomes saturated, recombination through state 2 can occur. Unfortunately, we were not able to measure the capture cross section for this state in p-type material. In n-type material, σ_{n2} was a factor of 20 less than σ_{n1}. If the relative sizes of the capture cross section remain the same in p-type material, recombination through state 2 will be negligible.

The O donor may be a more effective trap in n- than in p-type materials. The addition of O donors of density N changes the minority-carrier lifetime τ_p to τ_p', where

$$1/\tau_p' = 1/\tau_p + N\sigma_{p2}v_p \ . \tag{25}$$

For $N = 0.9\times10^{16}$ cm^{-3}, the largest value N in n-type material reported in Paper I, $\sigma_{p2} > 3\times10^{-17}$ cm^2 and $v_p = 2\times10^7$ cm/sec^{-1}, the change in reciprocal minority-carrier lifetime is

$$N\sigma_{p2}v_p > 5\times10^6 \text{ sec}^{-1} \ .$$

Thus the minority-carrier lifetime due to O donors will be less than 200 nsec. The minority-carrier lifetime due to O may be much shorter than this since we can only establish a lower bound to σ_{p2}

The recombination through O is readily saturated because σ_{n2} is small. The hole concentration at which saturation occurs can be calculated by equating the rates for electron and hole capture:

$$\sigma_{p2}v_p p n_2 = \sigma_{n2}v_n n(N - n_2) \ . \tag{26}$$

State 2 is half-saturated when $n_2 = \frac{1}{2}N$. If $v_p \approx v_n$, the hole concentration at half-saturation is

$$p_{1/2} = (\sigma_{n2}/\sigma_{p2})n \ . \tag{27}$$

If $\sigma_{p2} = 3\times10^{-16}$ cm^2 (a value of σ_{p2} 10 times greater than the lower bound and giving a hole-minority-carrier lifetime of 20 nsec), $n = 5\times10^{17}$ cm^{-3}, and $\sigma_{n2} = 10^{-19}$ cm^2, the hole concentration at saturation is $p_{1/2} = 1.7\times10^{14}$ cm^{-3}. Such an injected hole concentration would be achieved at a junction current of about 1 mA.

VIII. EVIDENCE THAT CENTER BEING STUDIED IS ISOLATED SUBSTITUTIONAL O DONOR

The O donor was first observed in donor-acceptor pair-line spectra at 1.6 K by Dean *et al.*[7] Exceedingly clean pair-line spectra were observed. The analysis of these pair spectra unambiguously showed that O is a deep donor with a binding energy of 0.895 eV and that O is substitutional for P. Bhargava[8] and Dishman[9] later showed that as the temperature of the sample is raised, the pair recombination changes to O donor-free hole recombination, the latter being dominant above 120 K. Recently, Jayson *et al.*[6] measured the decay of this luminescence at room temperature for a number of samples with different carrier concentrations. An average of their results indicates that the free-to-bound luminescence decays in about 46 ± 14 μsec at $p = 2.5\times10^{17}$ cm^{-3}.

We find that state 1 has a binding energy of ≈ 0.88 eV, in agreement with Dean *et al.*[8] Our lifetime measurements for this state gave $\tau_{p1} \approx 46\pm5$ μsec for $p = (2.5\pm0.7)\times10^{17}$/cm^3. This is in good agreement with the lifetime measured by Jayson *et al.*[6] On the basis of having approximately the same lifetime and energy level, we conclude that state 1 is the same state that gives rise to the free-to-bound luminescence associated with O and that this is a state of isolated O on a P site.

IX. SUMMARY

We have measured the recombination properties of the O donor in a series of experiments in which light irradiation is used to prepare the O centers in a diode depletion layer in a specific initial charge state, the diode is pulsed to cause electron or hole capture, and photocapacitance measurements are used to determine the change in the charge state. We proved that state 2 is a two-electron state of the O donor. Unlike other donors in GaP, the recombination of the two-electron state with a hole shows no Auger recombination. This is consistent with our finding that both electrons in state 2 are deeply bound. The capture cross sections were measured for electrons and holes into both states. The lifetime of the first electron in the p-type ($p \approx 2.5\times10^{17}$ cm^{-3}) material is about 46 μsec and agrees with previous luminescence experiments. The second electron recombines in less than 5 nsec. This is consistent with our picture that the electron in state 2 is close to the valence band and recombines nonradiatively. The electron-capture cross sections in n-type material were measured. It was found that the capture cross section of the second electron is 20 times smaller than that of the first electron. The capture cross section of the first electron was measured in both n- and p-type material. Both experiments gave about 2×10^{-18} cm^2. Using the electron-capture cross section of state 1, the maximum O donor concentration reported in Paper I, and a minority-carrier lifetime of 13 nsec, we estimate that only about 1.5% of the recombination is through the O center in p-type material. The center under study is chemically identified as the substitutional O donor by comparing the results of luminescence studies of this donor with our photocapacitance measure-

ments of the energy level and lifetime of the electron in state 1.

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Infrared Absorption of Localized Longitudinal-Optical Phonons

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A new type of localized vibrational mode is shown to occur near donors and acceptors in polar semiconductors. In general, the mode appears in a solid with infrared-active lattice vibrations when an impurity center with appropriate electronic transition energies is introduced by doping. The polarizability of the center perturbs the dielectric function locally, shifting the longitudinal-optic phonon. Infrared-reflection data showing the new localized mode are presented for GaP and GaAs. A macroscopic Clausius–Mosotti-type theory is developed for the effective dielectric function of the solid including the spheres. This theory yields good fits to the Raman data of Dean *et al.* and to the present infrared data.

I. INTRODUCTION

Though localized vibrational modes have been studied experimentally for only ten years, a great deal of information has been accumulated for modes in almost every type of crystal system. The most common situation which leads to a localized mode occurs when one of the host atoms of a crystal is replaced by an impurity atom of ligher mass.[1,2] With this replacement there is usually a new vibrational mode of the crystal with frequency above that of all host-lattice modes, and whose eigenvector has most of its amplitude on the impurity atom.[2] The model for such a mode is microscopic, involving the mass change at the impurity site and possibly force-constant changes for the bonds linking the impurity to the neighboring host atoms. In contrast to this microscopic type of local mode, this paper presents a theoretical and experimental study of a localized mode involving a group of host atoms near an impurity. The group of atoms is influenced by the presence of an impurity because of its special electronic properties.

Dean *et al.* were the first to observe this new type of localized vibrational mode. They observed the mode in the Raman spectrum of donor impurities in gallium phosphide.[3] The same modes have recently been detected by infrared techniques.[4] In the present paper we study the absorption of these modes by infrared reflectivity and present a macroscopic dielectric theory for their frequency and line shape. In addition, the Raman scattering strength is derived from the theory and compared with the Raman spectra. For either the infrared or Raman activity of this type of localized mode we adopt a point of view quite different from that of the microscopic defect model. As an example consider the donor sulfur (S) replacing a P ion in GaP. Such a replacement might lead to a localized mode of the microscopic type though it has not yet been observed. Such a mode need not concern us further. If the GaP crystal is cooled, the extra electron of the donor is no longer thermally excited into the conduction band. It resides in the 1S level of the donor. This bound electron is polarizable and thus changes the dielectric function of the medium in its vicinity. It is this extra polarizability, which we describe mac-