

Recombination Cross Section for Holes at a Singly Ionized Copper Impurity in Germanium*

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The recombination cross section has been measured for several copper-doped-germanium samples from the decay of the photoexcited-carrier population. Measured carrier lifetimes were sufficiently long to ensure that the photoexcited carriers were in thermal equilibrium with the lattice. The magnitude and temperature dependence of the cross section indicate that recombination occurs via acoustic-phonon emission for excited-state capture, and optical-phonon emission for capture directly into the ground state. Cross sections reported in this work are an order of magnitude larger than those measured from generation-recombination noise.

I. INTRODUCTION

The recombination cross section for thermal holes at a singly ionized copper acceptor in germanium has been measured from the photoconductive-signal decay. A carbon dioxide laser was pulse modulated with an external GaAs modulator to produce an excess hole population in the copper-doped-germanium sample. The carrier lifetime was then measured by observing the decay of the photosignal. Careful determination of the compensating donor density¹ and photoexcited-carrier concentration was made by Hall analysis and resistivity measurements. Samples measured had lifetimes at least an order of magnitude greater than the time required for thermalization of the photoexcited carriers.² Therefore, even though the photon energy was much greater than the energy required to ionize the neutral-copper centers, capture did not occur until the carriers had come into thermal equilibrium with the lattice. Consequently, these results can be compared directly with theoretical calculations based on an assumed Boltzmann distribution.

Lax³ has given a classical theory for recombination at impurity centers, for both acoustic- and optical-phonon-emission processes. This classical theory was modified by Hamann and McWhorter⁴ for the acoustic process. A quantum-mechanical calculation for capture via acoustic-phonon emission has been made by Ascarelli and Rodriguez,⁵ and a revised version has been given by Brown and Rodriguez.⁶ In the quantum theory, the recombination cross section is defined as

$$\sigma_r = \sum_{n=1} P_n \sigma_c(n), \quad (1)$$

where $\sigma_c(n)$ is the capture cross section for the n th bound state, and P_n is the probability that a carrier captured into the n th state will not be ionized.

The decay of an excess carrier population can be written⁷

$$\frac{dp}{dt} = -\langle v \rangle p N^- \sum_{n=1} \sigma_c(n) + \sum_{j=1} \beta_j N_a(j). \quad (2)$$

Here, the first term is the rate of removal of holes from the band, and the second term is the rate of thermal ionization from bound states. The term β_j is the thermal-ionization probability per unit time from bound state j , and $N_a(j)$ is the density of bound holes in the j th state. It is common practice for the capture and ionization terms to be combined to give the usual solution for $p(t)$:

$$p = p_0 e^{-t/\tau}, \quad (3)$$

where

$$\tau = (N^- \langle v \rangle \sigma_r)^{-1}. \quad (4)$$

This solution ignores the delay between capture and ionization for the $(1 - P_n)$ fraction of carriers which are captured into state n . We will comment on this later. The experimental cross section is defined as

$$\sigma = (N^- \langle v \rangle \tau)^{-1}, \quad (5)$$

where $\langle v \rangle$ is the average thermal hole velocity, N^- is the density of ionized recombination centers, and τ is the measured decay time. For a thermal distribution, $\langle v \rangle = (8kT/\pi m^*)^{1/2}$, where m^* is the effective mass of the carriers.

II. EXPERIMENTAL DETAILS

Previous publications¹ have given the details of the determination of compensation and doping levels for the samples used in this work. The results are summarized in Table I.

A carbon dioxide laser, having an output power of about 2 W at 10.6 μm was used to excite excess carriers in the copper-doped-germanium samples. A GaAs electro-optic modulator,^{8,9} external to the laser cavity, was mounted in the transmission line from a high-voltage pulser (Spencer-Kennedy model 503) to a 50- Ω termination. Figure 1 shows a view of the modulator mount and stripline. This type of system has been described by Bridges,

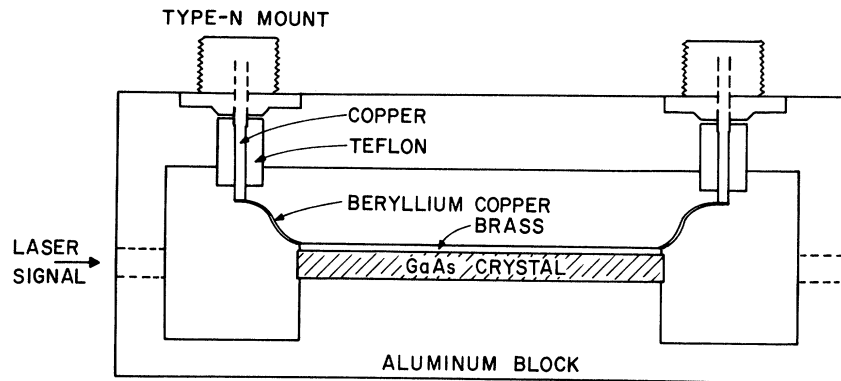


FIG. 1. Stripline mount for GaAs electro-optic modulator.

Chang, and Cheo.¹⁰ We used a 50- Ω load (Bird Electronic Corp., model 8130) which was specially modified to handle the 20-kW peak power from the pulse generator. The direction of polarization of the laser beam was aligned parallel to the applied electric field. The laser output was partially self-polarized by an internal Brewster window. A diagram of the experimental setup and bias circuit is shown in Fig. 2. An X-Y recorder was used to record the sampling oscilloscope traces for analysis.

To provide a matched output from the samples

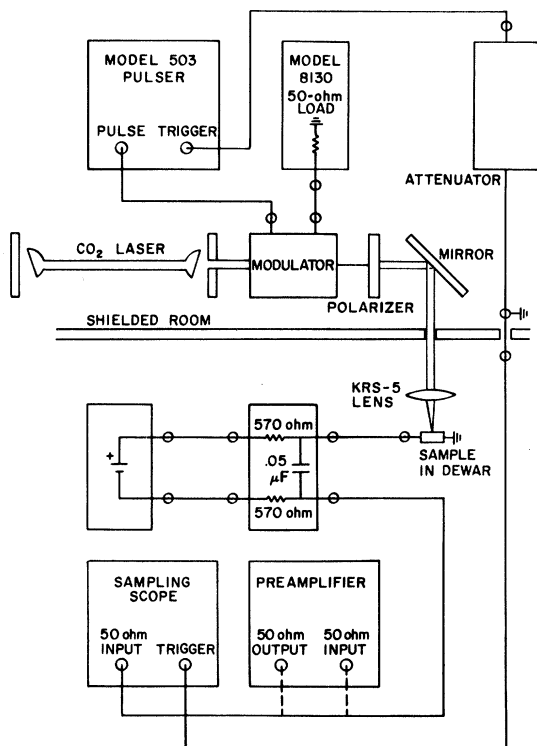


FIG. 2. Circuitry for nanosecond-time-constant measurements.

mounted on the copper cold finger of the helium Dewar, a 50- Ω beryllium-copper coaxial line was installed, running through the liquid-helium chamber. The samples, cut from the same crystal slice as the Hall sample, were soldered to copper screws and screwed into a gold-plated integrating cavity having a window to admit the laser beam. The temperature of the mount was varied with a resistance heater and monitored with a calibrated carbon resistance thermometer.

Since it was important to know the number of carriers generated with the laser signal on the sample, the circuit bias voltage and current were recorded along with the maximum output pulse voltage across the load resistor. Using the sample dimensions and mobility, the output-voltage changes could then be converted into carrier-concentration changes. The data of carrier concentration as a function of time were fit to a model of the decay by computer. The signal decay was used for this analysis, and the computer normalized all decay curves to unity at the start of the decay. Care was taken to keep the carrier concentration much less than the compensation density. Thus, the recombination-center density was nearly equal to the density of donors. For the laser circuit we found

$$p = \frac{l/wt}{e\mu} \frac{1 + 50j_0/V}{50j_0 R_0/V - 50} \quad (6)$$

where l/wt is the ratio of the sample length (between electrodes) to the width and thickness. The sample mobility is given by μ , e is the electronic

TABLE I. Summary of sample properties.

Sample	N_d (cm^{-3})	N_d (cm^{-3})
143.13	2.1×10^{13}	4.3×10^{10}
143.1 ^a	1.8×10^{13}	5.8×10^{10}
145.1	2.7×10^{13}	1.9×10^{11}
146.1	5.9×10^{13}	2.5×10^{12}

^aMeasurements of J. Stannard (unpublished).

charge, j_0 and R_0 are the bias current and sample resistance (pulse off), and V is the output voltage across the load resistor. This is valid as long as the pulse is short enough so that the $0.05\text{-}\mu\text{F}$ capacitor cannot discharge appreciably, a condition which was easily fulfilled.

Two preamplifiers were used, one with a rise time less than 4 nsec, the other with a rise time of about 20 nsec.¹¹ The modulated pulse itself decays in about 0.5 nsec or less, so that the preamplifier was the limiting feature of our setup.

The photo-Hall effect was used to analyze the temperature dependence of the carrier lifetime. For photoexcitation, the carrier concentration p is equal to $G\tau$, where G is the optical generation rate. It can be assumed that G is independent of temperature, so that the carrier concentration is proportional to the carrier lifetime. This assumption is verified by comparison of the direct lifetime measurements with the photo-Hall results.

III. EXPERIMENTAL RESULTS

A determination of the lifetime requires that all transient effects which may mask or distort the signal produced by the changing carrier concentration be separated out. These effects are of two basic types, those arising out of the circuitry itself and those produced by other physical phenomena within the sample. The circuitry used for the time-constant measurements was carefully checked to make certain that there was no appreciable distortion in the transmission line. Careful attenuation, shielding, and grounding were employed to eliminate pickup of the pulser current in the detecting circuit, so that maximum amplifier gain could be used without difficulty. With the faster preamplifier alone, signals with peak voltage on the order of $100\ \mu\text{V}$ could be measured. With the slower preamplifier as the first amplification stage, signals of $20\ \mu\text{V}$ were easily recorded. It was necessary to have this sensitivity so that measurements could be made down to the limit of low bias, where the applied electric field does not heat the carrier distribution. All the measurements were made for a range of electric field strengths to make certain that the low-field limit had been reached.¹²

Two effects associated with the sample itself can sometimes alter the signals produced by the generation and recombination of carriers. First, it is important to have the dielectric relaxation time much shorter than the photocarrier recombination time.¹³⁻¹⁶ The dielectric relaxation time is given by

$$\tau_{\text{dielec}} = \epsilon \epsilon_0 \rho,$$

where ϵ is the dielectric constant of the sample (16 for germanium), ϵ_0 is the permittivity of free

space, $8.85 \times 10^{-14}\ \text{F/cm}$, and ρ is the sample resistivity. For germanium we have $\tau_{\text{dielec}} = 1.4 \times 10^{-12} \rho\ \text{sec}$, where ρ is in $\Omega\ \text{cm}$. Using the CO_2 laser, we have had no problem keeping the dielectric relaxation time much shorter than the carrier lifetime since the resistivity under measurement conditions was always quite low. Samples 146.1 and 145.1 had background resistivities on the order of 100 and 400 $\Omega\ \text{cm}$, respectively, under measurement conditions,¹⁷ giving dielectric relaxation times of 1.5×10^{-10} and 6×10^{-10} sec in each case. Therefore, dielectric relaxation was not a limiting feature of the measured response times.

Another problem which must be considered is the importance of photovoltaic signals which may result from contacts or inhomogeneous illumination of the sample, etc. This was easily checked with our circuit, since any signal coming from the sample would still pass through the coupling capacitor and on to the preamplifier even in the absence of bias. With maximum gain we have not seen any photovoltaic signals with amplitudes greater than 10% of the photoconductive signal. Even this may have been due to coupling from the pulser through the trigger cable. In most cases, there was no detectable signal in the absence of bias.

Time-constant data for sample 146.1 are presented first. Measurements were made at six temperatures between 3.13 and 29.5 K, for electric fields in the range of 0.16 to 25 V/cm. Typical photocarrier concentrations for the CO_2 laser background were about $2 \times 10^{11}\ \text{cm}^{-3}$, with the modulated pulse producing an additional $4 \times 10^{10}\ \text{cm}^{-3}$.¹⁸ Since this average concentration is an order of magnitude smaller than the density of compensating donors, only a small correction to the recombination-center density was necessary. Our method for determining the carrier concentration is as follows: The sample was precooled at 77 K, and its resistance was measured before transferring liquid helium. Knowing the sample resistance at 77 K, we computed the dimension ratio l/wt from the resistivity value determined by the Hall measurement at 77 K. Under pulse-measurement conditions, the dimension ratio was used together with the mobility (taken from photo-Hall measurements) and sample resistance to calculate the carrier concentration.

Figure 3 shows the signal measured for sample 146.1 at 3.13 K with a bias of 0.16 V/cm.

The low-bias values of the decay time are shown in Fig. 4 and compared with the temperature dependence of the photo-Hall carrier concentration, normalized at 10 K. The temperature dependence is seen to match within experimental uncertainty. We therefore find justification for the generally assumed relationship that the optical generation

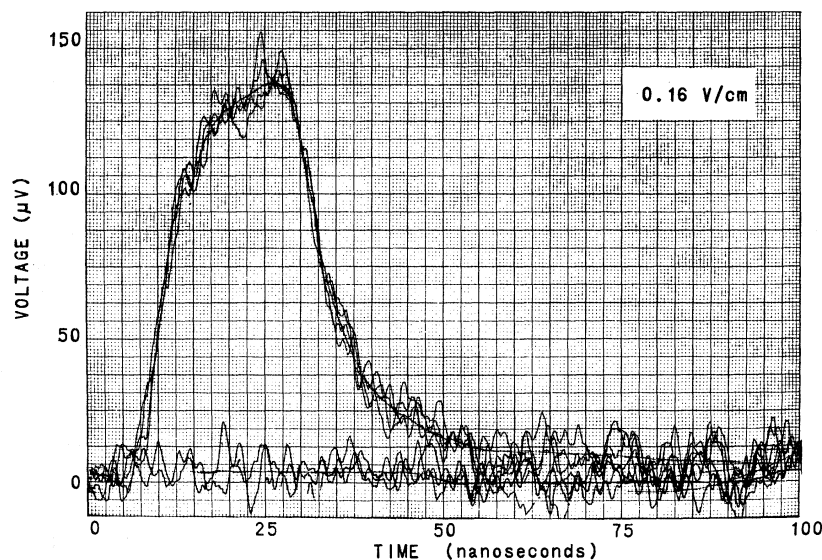


FIG. 3. Response of sample 146.1 at 3.1 K to a 20-nsec pulse from a CO_2 laser. Bias on the sample was 0.16 V/cm, and the peak voltage across the 50- Ω load was 135 μV . Lower trace shows zero-bias response.

rate G is independent of temperature.

Sample 145.1 was measured at two temperatures, 4.3 and 19.6 K, over a range of electric fields from 0.07 to 15 V/cm. Measurement conditions at 4.3 K produced about $2 \times 10^{10}\text{-cm}^{-3}$ photocarriers and the pulse introduced an additional $5 \times 10^9\text{ cm}^{-3}$. At 19.6 K, the photocarrier concentration was $4 \times 10^{10}\text{ cm}^{-3}$ at low bias, with the pulse adding about $5 \times 10^9\text{-cm}^{-3}$ additional carriers. With a donor concentration of $1.9 \times 10^{11}\text{ cm}^{-3}$, the recombination-center density was found to be 2.1×10^{11} and $2.3 \times 10^{11}\text{ cm}^{-3}$ at 4.3 and 19.6 K, respectively. Figure 5 compares the low-bias values of the direct lifetime with the photo-Hall temperature dependence for sample 145.1. The difference in recombination-center density was accounted for in the lifetime values plotted (we have

renormalized them to values appropriate for $1.9 \times 10^{11}\text{-cm}^{-3}$ recombination centers). Once again the two different techniques are seen to give the same temperature dependence.

Two slices from a third crystal, 143.13 and 143.1, have been measured with a different system, developed by Stannard.¹⁹ This system uses an InAs emitter at $3.1\text{ }\mu\text{m}$ to excite the photocarriers. A single measurement was made at 24 K for sample 143.13 and the same system was used by Stannard to measure sample 143.1 over a wider temperature range. The background carrier concentration at 24 K was $5.6 \times 10^9\text{ cm}^{-3}$, while the pulse produced less than $1 \times 10^9\text{-cm}^{-3}$ additional carriers.

In Fig. 6 we show the measured cross section for the four samples studied. A value of $0.33m_0$

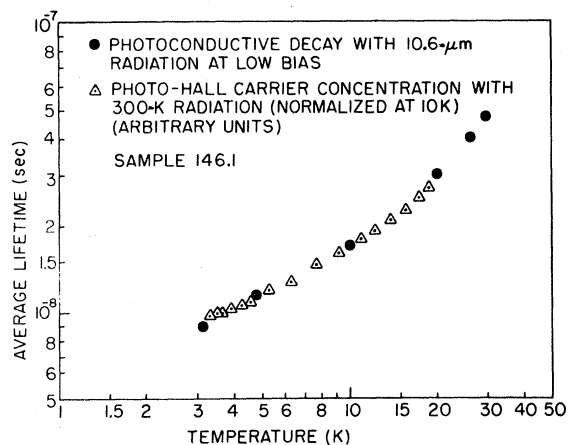


FIG. 4. Comparison of the temperature dependence of the photo-Hall carrier concentration with the direct lifetime measurement in the limit of low bias, for sample 146.1.

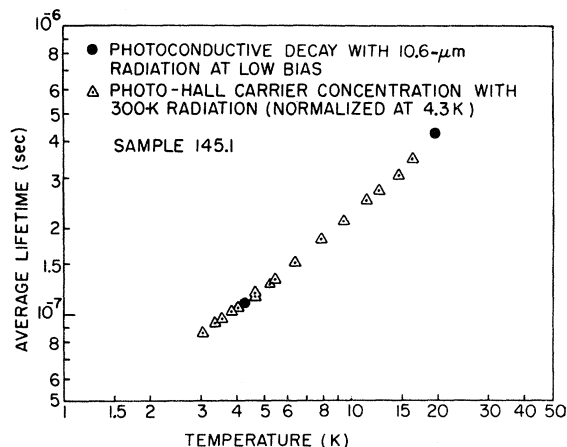


FIG. 5. Comparison of the temperature dependence of the photo-Hall carrier concentration with the direct lifetime measurements in the limit of low bias, for sample 145.1.

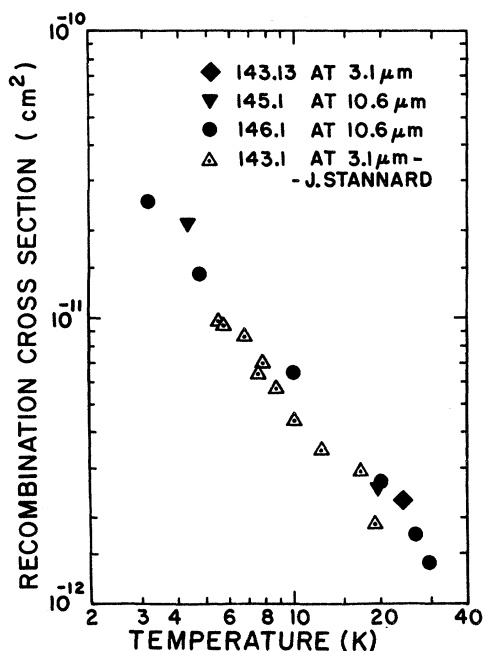


FIG. 6. Recombination cross section for copper-doped germanium as a function of temperature. Data for sample 143.1 were measured by Stannard (Ref. 19).

was used in calculating the average thermal velocity of the carriers. Since the theory of Lax predicts a cross section which depends on m^{*2} , we expect the heavy holes to recombine much more rapidly than the light holes. Light-hole recom-

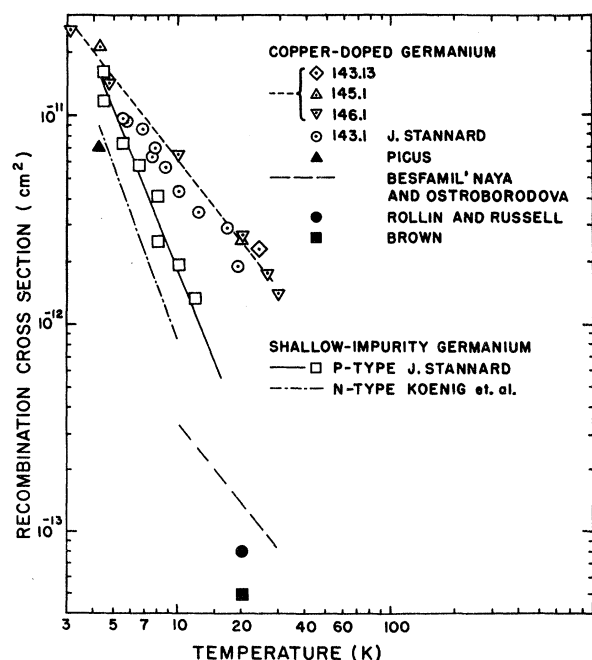


FIG. 7. Summary of experimental recombination cross sections for copper-doped germanium. Experimental values for shallow acceptors and donors are also shown.

bination should occur via interband scattering²⁰ into the heavy-hole band, over the range of temperature and carrier lifetimes studied. At lower temperatures or higher compensation densities, light holes may live appreciably longer than heavy holes. Values of the cross section are seen to be in good agreement for all four samples. Considering the problems involved in determining both N_A and the carrier lifetime, the agreement between the four samples is very satisfactory. This agreement was gratifying since the range of compensation involved varies by a factor of 50. It should be noted that the measurements made on samples 143.13 and 143.1 were performed at a shorter wavelength, and that the circuit used in that case was different from the one shown in Fig. 2.

IV. COMPARISON WITH OTHER EXPERIMENTS

Carrier lifetimes have been measured by several authors for copper-doped germanium below 30 K.²¹⁻²⁴ Three of these measurements are in fair agreement with each other, but differ from our result by more than an order of magnitude. Two measurements are in much better agreement. One of these by Stannard is included in our experimental results; the other, by Picus,²² differs by a factor of 3 from our result. Measurements of the capture cross section for copper impurities are listed in Table II, and displayed in Fig. 7. It may be coincidental that the three results near 1×10^{-13} cm² at 20 K were all obtained from generation-recombination (gr) noise measurements. In the case of Besfamil'naya and Ostroborodova,²⁴ we expect their values to be too small by a factor of 2, since they analyzed their Hall data with an assumed degeneracy factor of 2.²⁵ Even with this correction, their result is an order of magnitude lower than our value at 20 K. While time constants measured by the noise method might not be fundamentally comparable to photoconductive-decay measurements, there is evidence that one of the noise measurements was influenced by dielectric relaxation effects. Although the paper by Besfamil'naya and Ostroborodova does not mention the resistance of their samples under test conditions,

TABLE II. Summary of experimental measurements of the cross section for hole capture at a singly ionized copper acceptor in germanium.

T	Cross section (10^{-13} cm ²)	Reference
4.2	200	This paper; Stannard (unpublished)
20	25	
4.2	69	Picus (Ref. 22)
20.	0.5	Brown (Ref. 21)
20.	0.8	Rollin and Russell (Ref. 23)
20.	1.4	Besfamil'naya and Ostroborodova (Ref. 24)

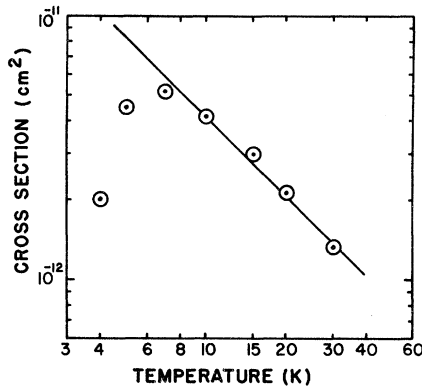


FIG. 8. Cross section for optical-phonon recombination, determined by subtracting the cross section for shallow acceptors from the cross section for copper-doped germanium. The T^{-1} temperature dependence predicted by Lax (Ref. 3) is shown as a solid line. The absolute value of the theoretical cross section for optical-phonon recombination is about a factor of 40 smaller. Experimental results below 8 K are thought to be unreliable for reasons discussed in text.

we can estimate the resistivity in one case from their measured values of carrier density with and without illumination. Assuming a carrier mobility of about 2×10^5 cm²/V sec at 23 K, the resistivity of their sample was approximately 3×10^5 Ω cm in the dark, and 6×10^4 Ω cm under illumination. The calculated dielectric relaxation times then turn out to be 4×10^{-7} and 8×10^{-8} sec, respectively. Since their measured response times are between these two values, we feel that their measurements were strongly influenced by the dielectric relaxation time.²⁶

The results of Brown at 20 K show variations in the measured cross section between 1.3×10^{-14} and 1.7×10^{-13} cm² for five samples having the same compensation. Although dielectric relaxation effects could have played a role, in some cases the sample resistivity was low enough so that some other explanation is needed.

We have included the results of Koenig, Brown, and Schillinger²⁷ for *n*-type germanium in Fig. 7. Shallow levels show a slightly steeper temperature dependence of the cross section than copper-doped germanium. The data on our purest copper-doped-germanium sample, 143.13, show a $T^{-1.6}$ dependence of the cross section. A shallow *p*-type level measured by Stannard gave a $T^{-2.3}$ dependence,²⁸ while photo-Hall data on a *p*-type shallow level we have measured indicates a dependence of $T^{-2.1}$.

We can propose an explanation for the difference in temperature dependence between shallow acceptors and copper. As can be seen in Fig. 7, the cross sections we have found for copper-doped germanium are larger than those for shallow acceptors. Since the excited-state spectrum is identical for both copper and shallow acceptors,^{29,30} it

could be expected that acoustic-phonon recombination would be identical for both types of impurities. This is because capture directly into the ground state is negligible, even for shallow impurities. However, because the copper ground state is deeper than the optical-phonon energy, the cross section for copper may be larger due to contributions from recombination via optical-phonon emission. At low temperatures, the optical-phonon-recombination theory of Lax predicts a T^{-1} dependence of the cross section. When both optical and acoustic capture is involved, the decay of an excess carrier concentration can be written

$$\frac{dp}{dt} = -\langle v \rangle p N^- \sum_{n=1} P_n [\sigma_c(n)_{\text{opt}} + \sigma_c(n)_{\text{acous}}], \quad (7)$$

since P_n will be independent of the type of phonon emitted. We can ignore optical-phonon capture into all states except the ground state, since the difference between the carrier energy and the excited-state energies will be much less than the optical-phonon energy. Therefore, the cross section for copper-doped germanium will be equal to the acoustic-phonon cross section, plus the cross section for capture into the ground state via optical-phonon emission. By subtracting the cross section measured for shallow *p*-type acceptors from the cross section determined for copper-doped germanium, we obtain the optical-phonon cross section. The result is shown in Fig. 8. For temperatures greater than about 7 K, we see an approximate dependence of T^{-1} , as predicted by Lax. At lower temperatures, the agreement fails. This is probably due to slight inaccuracies in the two measurements, and the use of a simple T^{-n} dependence of the cross section with temperature. The results of Brown and Rodriguez for shallow donors show that the temperature dependence of acoustic-phonon recombination decreases in the temperature region below 6 K. More accurate measurements of the cross section in this lower-temperature region will be needed to verify this prediction.³¹

It is also possible to understand the slightly greater value found for the cross section of shallow acceptors compared with donors. The theory of Lax predicts a cross section proportional to $(m^*)^2$, and this correctly accounts for the experimental difference.³² A different degeneracy factor might destroy this agreement, but the discussion of this point by Brown³³ indicates that we cannot easily draw a conclusion about the degeneracy appropriate for electron recombination.

Blakemore³⁴ has proposed a correction to the measured cross section, to account for the mean free path of the carriers being comparable to or less than the average separation between capture centers. The cross-section correction factor is given as $[1 + (\pi/8\lambda)(N_d + p)^{-1/3}]$, where λ is the mean free path of the carrier. We have calculated this

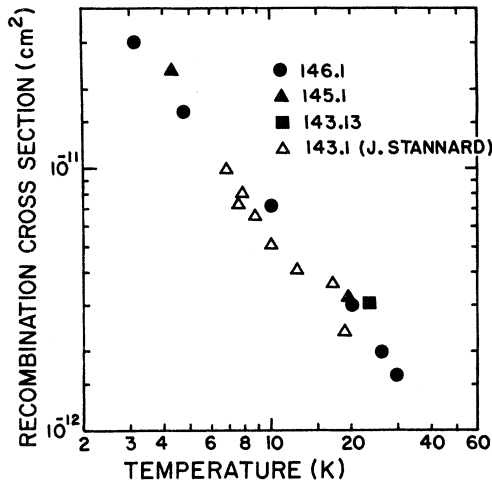


FIG. 9. Recombination cross section for copper-doped germanium as a function of temperature, after making the correction proposed by Blakemore (Ref. 34). The corrected values are 10–30% larger than the results shown in Fig. 6.

correction factor for samples 143.13, 145.1, and 146.1, and listed the results in Table III. These corrections, when applied to the cross sections given in Fig. 6, yield a slight improvement in the agreement between the four samples. We assumed that the correction for 143.1 was identical to that of 143.13. The corrected cross sections are shown in Fig. 9.

V. COMPARISON WITH THEORY

The theory of acoustic-phonon recombination has been compared with experiment for shallow donors.^{3–6,27} Both the classical theory of Lax and the quantum theory as developed by Brown and Rodriguez give values for the cross section that are too low. The quantum theory was deliberately minimized, so that it may yield closer agreement if it is recalculated with larger values for the velocity of sound, and if more terms are added to include excited states for n greater than 7.

For the case of optical-phonon recombination, the theory of Lax predicts a cross section at 10 K of about 1×10^{-13} cm². In calculating this, we have used his numerical result for silicon, a value of 0.037 eV for the optical-phonon energy, and the heavy-hole mobility given by Brown and Bray³⁵ for acoustic scattering. Also used are the ratio of optical to acoustic deformation potentials, given by Brown and Bray, and the appropriate dielectric constant for germanium. The experimental cross section for optical-phonon recombination is a factor of 40 greater than the theoretical prediction.

There has been no attempt to formulate a detailed recombination model for p -type germanium. The excited-state spectrum assumed in the quantum theory is hydrogenic and does not correspond

to the spectrum of acceptor states. Another difficulty is the degenerate nature of the valence band, making it necessary to consider interband scattering for a comprehensive treatment.

The comparison of experiment and theory may be further complicated in the event that future experiments are performed on samples having carrier lifetimes of less than 10^{-8} sec. Aside from the difficulty in producing thermal carriers when the carrier lifetime is equal to or shorter than the thermalization time,² the reionization of carriers from excited states will occur after a relatively large delay time. The correct expression for the decay of an excess carrier concentration was given in Eq. (2). To estimate the delay between capture and subsequent ionization of the $(1 - P_j)$ fraction of carriers captured into state j , we note that the minimum delay will be $(\beta_j)^{-1}$. Consider a population of carriers, p_0 at $t=0$, the start of the decay. Of these, p_1 will be captured permanently the first time they enter a bound state, while p_2 will be captured and ionized at least once before they finally recombine. The fraction p_2/p_0 is given by

$$\frac{p_2}{p_0} = 1 - \frac{\sum_n \sigma_c(n) P_n}{\sum_n \sigma_c(n)} \quad (8)$$

The minimum average delay time, not counting any transitions among excited states before ionization, is

$$\langle \text{delay time} \rangle_{\min} = \frac{\sum_n \sigma_c(n) (1 - P_n) \beta_n^{-1}}{\sum_n \sigma_c(n) (1 - P_n)} \quad (9)$$

Using the results of Brown³³ we evaluate these quantities at 4 and 10 K, summing over the first-seven bound states. At 10 K, p_2/p_0 is equal to 0.67 with an average delay time of 5×10^{-10} sec; at 4 K, p_2/p_0 is equal to 0.18 with an average delay time of 7×10^{-9} sec. For carrier lifetimes in the vicinity of 10^{-9} sec, and at temperatures of less than 10 K, we can see that a significant percentage of the recombination centers will act as trapping centers. In this case, as has been pointed out by Lax, the decay of the excess carrier concentration will not be the simple exponential decay predicted in Eq. (3). Since carrier lifetimes as short as 3×10^{-10} sec have been recently reported for mercury-doped germanium,³⁶ it seems likely that a more exact treatment of the recombination process will be necessary.

Table III. Calculated cross-section correction factor (after Blakemore, Ref. 34).

Sample	Correction factor [1 + ($\pi/8\lambda$)($N_d + p$) ^{-1/3}]			
	3 K	10 K	20 K	30 K
143.13	1.11	1.18	1.30	1.44
145.1	1.12	1.11	1.18	1.26
146.1	1.18	1.12	•••	1.16

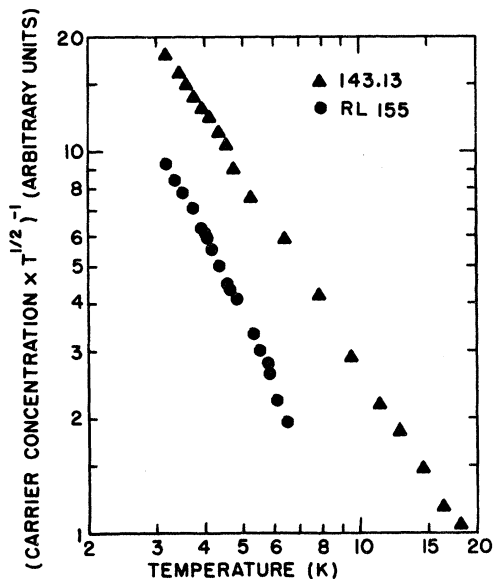


FIG. 10. The temperature dependence of the recombination cross section (proportional to $1/pT^{1/2}$) measured from the photo-Hall effect for a shallow acceptor and copper. Sample RL155 has an acceptor concentration of $3.7 \times 10^{11} \text{ cm}^{-3}$ and a compensation density of $3.0 \times 10^{11} \text{ cm}^{-3}$.

Recent studies of photothermal ionization are particularly helpful in indicating where improvements in the present theory are needed. Lifshitz, Likhtman, and Sidorov³⁷ have used these studies to compare the theoretical sticking probability calculated by Lax with their experimental results for shallow p -type acceptors. The experiment and theory were seen to agree for the D line (ionization energy 2.4 meV), but the experimental sticking probabilities were larger than those predicted by Lax for the C line and B line (ionization energies of 1.7 and 1.0 meV, respectively). In the case of the B line, the experimental values were about twice those predicted by theory. Since the values of $\sigma_c(n)$ are largest for large values of n , an increase in the sticking probability for these states will substantially increase the recombination cross section.⁴ In the case of optical-phonon recombination, which occurs in copper-doped germanium, the sticking probability for the ground state is already very close to unity, so that some other explanation is needed to resolve the discrepancy between experiment and theory.

Another interesting result from the measurements by Lifshitz *et al.* is that the sticking probabilities are large for the B , C , and D lines. The B , C , and D lines correspond to the $3p^{(2)}$, $3p^{(1)}$, and $2p^{(2)}$ states in the notation of Mendelson and James.³⁸ Therefore, it cannot be assumed that only s states are important in considering the recombination of holes in p -type germanium. Even if capture into p states were negligible, they would

still contribute to the cross section through the transition rate between bound states and ionization into the valence band.

The leveling off of the temperature dependence of the cross section at the lowest temperatures in some samples may be due to excited-state overlap or the effects of impurity-hopping conduction as proposed by Brown.³⁹ Photo-Hall measurements of the carrier concentration of sample 143.13 do not show any leveling off, even down to 3 K. Hopping conductivity in this sample should be very small, since the acceptor density is less than 10^{14} cm^{-3} . We have also measured a shallow p -type sample, with an acceptor concentration of less than 10^{12} cm^{-3} . The photo-Hall carrier concentration for this sample and sample 143.13 are shown in Fig. 10 as a function of temperature. We have graphed the inverse carrier concentration multiplied by $T^{-1/2}$, which should be proportional to the recombination cross section. The absence of any leveling off in both samples may be due to a lack of impurity conduction of the hopping type, or a failure of the excited-state radii from adjacent recombination centers to overlap, or both. In either case, it is interesting to note that the leveling off observed by Koenig *et al.*²⁷ does not occur in purer samples.

Possible contributions due to Auger recombination have been considered. Koenig, Brown, and Schillinger report a cross section for Auger recombination on the order of $2 \times 10^{-24} n \text{ cm}^2$ for n -type germanium, where n is the electron concentration density. Since in this case the carrier energy was about 50 k , while the lattice temperature was only 6 K, the estimate of Lax⁴⁰ predicts a value 580 times larger for the cross section appropriate to thermal electrons. This gives a value of approximately $10^{-21} n \text{ cm}^2$ at 6 K. Hole densities in our experiments varied from about 2×10^{11} to less than 10^{10} cm^{-3} . Assuming a close similarity between the Auger process for both electrons and holes, we should have contributions to our cross sections of up to $2 \times 10^{-10} \text{ cm}^2$ at 6 K, based on the values quoted by Koenig *et al.* Since the measured cross sections are more than an order of magnitude lower, and do not depend on the hole concentration, we feel that Auger recombination was not important.⁴¹ Because the data of Koenig *et al.* were taken at very large electric fields, bordering the breakdown region, perhaps some other effect was responsible for the data which led to their large estimate of the Auger cross section. Another estimate of the Auger cross section has been made by Ascarelli and Rodriguez.⁵ At 4 K they find a cross section of about $10^{-12} (n/N_c) \text{ cm}^2$, where N_c is the density of states in the conduction band ($4 \times 10^{15} T^{3/2} \text{ cm}^{-3}$). Thus, according to this model, Auger recombination should be negligible for concentrations

less than about 10^{15} cm^{-3} .

VI. SUMMARY AND CONCLUSION

The recombination cross section for thermal holes at a singly ionized copper center in germanium is found to be $2.5 \times 10^{-12} (T/20)^{-n} \text{ cm}^2$, where n varies from 1.6 to 1.0 as the compensation density varies from 4×10^{10} to $2.5 \times 10^{12} \text{ cm}^{-3}$. This large cross section is due to both acoustic-phonon recombination into excited states, and optical-phonon recombination into the ground state. The optical generation rate is found to be independent of tem-

perature as expected. No evidence of Auger recombination was found, even for hole densities as high as $2 \times 10^{11} \text{ cm}^{-3}$.

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¹⁸No attenuation of the laser beam was used on sample 146.1. From the carrier density and lifetime we can estimate the power dissipation in the sample. Assuming one ionization for each photon absorbed, the power is $0.117 \text{ eV} \times p/\tau$ or $1.7 \times 10^{-20} p/\tau \text{ W}$. Thus for sample 146.1 at the lowest temperature we find a dissipation of about 0.4 W cm^{-3} , or about 10^{-3} W in the sample. At low bias the power due to joule heating was on the order of 10^{-6} W in the sample.

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