Determination of Compensation Density by Hall and Mobility Analysis in Copper-Doped Germanium*

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The carrier concentration and mobility, as determined from the Hall effect, have been analyzed on a computer for a series of copper-doped-germanium samples. Both types of analysis gave good agreement in determining the density of compensating donors over the range of 4×10^{10} to 6×10^{15} cm^{-3}. This agreement is good evidence in support of the theory of ionized-impurity scattering. It was found that neutral-impurity-scattering theory had to be modified to account for the nonhydrogenic nature of the copper impurity center. The degeneracy of the copper acceptor was found to be four, in agreement with the effective-mass calculation.

I. INTRODUCTION

The Hall effect has been studied in a series of copper-doped-germanium samples to determine the density of compensating donors. Although the Hall effect has been investigated extensively,[1-5] there has been no systematic measurement and analysis of Hall data for a group-I acceptor over a wide range of doping and compensation levels. In this study, copper concentrations between 2×10^{13} and 2×10^{16} cm^{-3} were obtained. The compensation density was varied systematically between 4×10^{10} and 6×10^{15} cm^{-3}. The compensation density was determined by analysis of both carrier concentration and mobility as a function of temperature, using curve-fitting techniques on a computer.[6] The resulting donor concentrations, determined from the application of each theory, could then be compared. Since many of the copper-doped samples were prepared by diffusion, the net donor density could also be measured before the introduction of copper. The over-all agreement between carrier concentration and mobility analysis over the entire range was excellent. This agreement in determining the compensation density is a strong argument for the validity of the mobility expressions, especially the scattering theory for ionized impurities. Our results, with certain modifications, can be extended to other deep acceptors in germanium.

II. EXPERIMENTAL DETAILS

Copper-doped germanium was prepared either by doping with copper during the growth process, or by diffusion of copper into n-type material.[7] Diffusion was done in sealed quartz capsules, partially backfilled with hydrogen gas. Samples were cut into 3-mm slices, electroplated with copper, and diffused long enough to ensure saturation. After quenching, the slice was lapped off on both sides to give a sample thickness of about 1 mm.

The Hall measurements were performed with standard potentiometric methods, or with a high-input-impedance electrometer when the sample impedance was greater than 10^5 Ω. Isolation of the sample was better than 2×10^{12} Ω from ground. Magnetic fields between 100 G and 20 kG were used as required. The temperature was monitored with calibrated platinum and carbon resistance thermometers.[8] Calibration was accomplished between 1.5 and 100 K by mounting a calibrated germanium thermometer[9] in place of the sample. Above 100 K, the platinum resistor was calibrated against a copper-constantan thermocouple. Data were not taken above 160 K, since the Hall factor cannot be properly accounted for outside the high-field limit. This will be discussed.

III. MEASUREMENT THEORY

An accurate knowledge of the carrier concentration as a function of temperature allows us to determine the four parameters N_a, N_d, E_a, and N_v/g from the expression[10]:

$$p(p + N_d)/(N_a - N_d - p) = (N_v/g) e^{-E_a/kT}, \qquad (1)$$

where the carrier concentration p is related to the acceptor density N_a, activation energy E_a, degeneracy g, and the density of compensating donors N_d. N_v is the density of states in the valence band, which for germanium is $1.09 \times 10^{15} T^{1.5}$ cm^{-3}, for $m^* = 0.37 m_0$. This model assumes a single acceptor level, and neglects excited states of the impurity. Since for copper-doped germanium the deepest excited state is an order of magnitude removed from the ground state, this is a good approximation. Also, our restriction to measurements below 160 K means that we can safely neglect the second and third acceptor levels of copper[4] and the split-off valence band.[11]

All measurements were made in the limit of low electric fields to avoid carrier heating. In order to stay in the high-magnetic-field limit where the Hall factor is equal to unity, magnetic

fields up to 20 kG were used. There are, however, several potential problems with the use of high magnetic fields. Landau levels may alter the density of states in the band at high fields,[12] and the activation energy of the impurity itself can shift in accordance with the theory of Yafet, Keyes, and Adams.[13] The experiments of Gallagher[14] on shallow acceptors indicate that the effect predicted by Yafet *et al.* may be important at temperatures below 30 K and for fields in excess of 20 kG. Our measurements were generally limited to temperatures above 15 K, especially in the case of low-mobility samples which required high fields in that temperature region. However, since copper has an activation energy about four times deeper than the shallow impurities studied by Gallagher, the magnetic shift in the ground-state energy is much less likely to affect the measurements in this temperature region. Another mechanism, impurity conduction of the hopping type,[15] did cause deviations from the high-field limit in the region below 20 K for heavily doped, heavily compensated samples. In our analysis of the carrier concentration and mobility, no data were used from the temperature region where these problems occurred.

The carrier concentration as a function of temperature, determined from the Hall effect, was fit to the equation for p by adjusting all four parameters. Since the variation in p is very large, the fit was performed by minimizing the sum of the squares of the difference between the logarithms of experimental and calculated values of carrier concentration. Several initial starting values were used in each case, and all resulted in the same final values of the four parameters.

Mobility analysis gives us another means to determine N_d, since at low temperatures the compensation density determines the number of ionized scattering centers. In calculating the mobility, however, we must include the contributions due to neutral impurities and lattice vibrations, as well as ionized impurities. In general, since each of these mechanisms has its own particular temperature dependence, we can separate the contributions of each in analyzing the temperature dependence of the mobility. Lattice scattering parameters have been determined by Brown and Bray[16] for p-type germanium. Our treatment, which is slightly different, is based on the theory given by Bir, Normantas, and Pikus[17] which includes interband scattering. This somewhat more complicated theory, for the case of acoustic-phonon scattering, can be reduced to a single unknown constant using the approximations outlined by Bir *et al.* We evaluated this constant by requiring the theory to agree with the experimental results of Brown and Bray at 77 K. Optical-phonon scatter-

ing was included using the theory and parameters published by Brown and Bray. With our more complex formulation, and after normalizing the acoustic theory at 77 K, we found a calculated lattice mobility of 2078 cm^2/V sec at 300 K, in good agreement with Brown and Bray.

Ionized-impurity scattering has been calculated using the expression given by Brooks,[18] Herring, and Dingle.[19] The merits of the several different theories for this type of scattering have been discussed by Sclar,[20] who also gives the range of validity for the approximations used in each case. We have assumed that the singly ionized copper center has the same scattering potential as a singly ionized shallow acceptor or donor. This is reasonable, since most of the contribution to the scattering cross section comes from large values of the impact parameter, that is, at considerable distance from the core potential.

Neutral-impurity scattering has been calculated by Erginsoy[21] and discussed by Sclar.[22] The approximations used in Erginsoy's treatment are valid in the range of temperature we have used. However, the results of Erginsoy are based on a hydrogenic model which is not appropriate for neutral copper impurities. An adjustable parameter A was therefore included in the neutral-impurity-scattering expression to account for the difference between the ground-state wave functions of copper and group-III acceptors.[23] Without this adjustable factor, we found that for heavily doped samples the neutral-impurity-scattering contribution would account for more than all of the scattering in certain temperature regions.

The four scattering contributions, acoustic and optical phonons and ionized and neutral impurities, were calculated separately for each band. Interband scattering was only included for acoustic phonons in accord with Bir *et al.* The mobility was then calculated by numerical integration (Simpson's rule), using the equations given by Bir *et al.* Three parameters were adjusted by the fitting program to obtain the least-squares difference between the logarithms of the measured and calculated values over the range of temperature measured, generally 20–160 K. It was felt that the value of N_a was known with enough precision to fix its value from the analysis of carrier-concentration temperature dependence. The three adjustable parameters were the donor density N_d, the scale factor multiplying the neutral-impurity-scattering time, A, and a third parameter G to account for any error in measuring the sample dimensions. This dimensional factor is a number close to unity, multiplying the calculated mobility. Although the sample thickness could be measured quite accurately, the width and length between resistivity probes was known only within about 5–10%. Without the
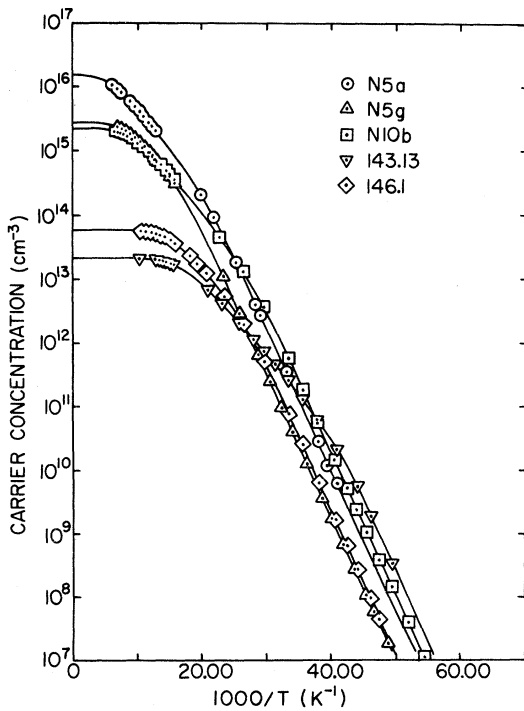
FIG. 1. Carrier concentration as a function of inverse temperature for five representative samples. Points show the experimental data; lines are drawn to show the calculated carrier concentration using the parameters determined in the fitting program.

adjustable factor to account for this error, the purest samples could not be fit with reasonable values of N_d, since the errors in geometrical measurement were comparable to the contribution of ionized-impurity scattering in these samples.

It should be mentioned that the two types of analysis, carrier concentration and mobility, need not in principle give equal values of N_d. Since some residual concentration of shallow acceptors is unavoidable in real material, the value of N_d as determined from mobility analysis will include those donors compensating the residual shallow acceptors. For the analysis of carrier concentration, only the compensated copper centers are important, so that the value of N_d in this case should be less than that determined from mobility analysis. In fact, we did not observe any such trend, even in the three samples which had donor concentrations less than 3×10^{12} cm^{-3}. It was therefore felt that the residual-shallow-acceptor concentrations were quite small in these samples.

IV. EXPERIMENTAL RESULTS

Carrier-concentration and mobility data are shown in Figs. 1 and 2 for five representative samples. Points show the experimental data, lines are drawn to show the calculated carrier concentra-

tion and mobility using the parameters determined in the fitting program. Table I gives the complete results for the samples measured. Some patterns in these results are evident. In the diffused samples, we see that calculated values of N_d agree closely with the measured concentration of N_d before diffusion in all cases where g is in the range of 4 to 6. In cases where the degeneracy is higher (samples N10a, N11g, N11i, RL174a, and RL174b), the values of N_d before and after diffusion do not agree as well. The activation energy of the samples with high-degeneracy values are also lower than expected for copper-doped germanium. We investigated the cause of this by taking a photoconductive spectral response on sample RL174a. The photoconductive signal was seen to extend to at least 40 μm, with a sharp decrease in intensity where the photon energy dropped below 0.04 eV. This indicates that a level with an activation energy of about 0.03 eV or less is present in addition to copper. To confirm this, the carrier-concentration temperature dependence was reanalyzed using a model for two acceptors and a donor.[24] The improved fit using this model is summarized in Table II for those samples which had unusual degeneracy values.

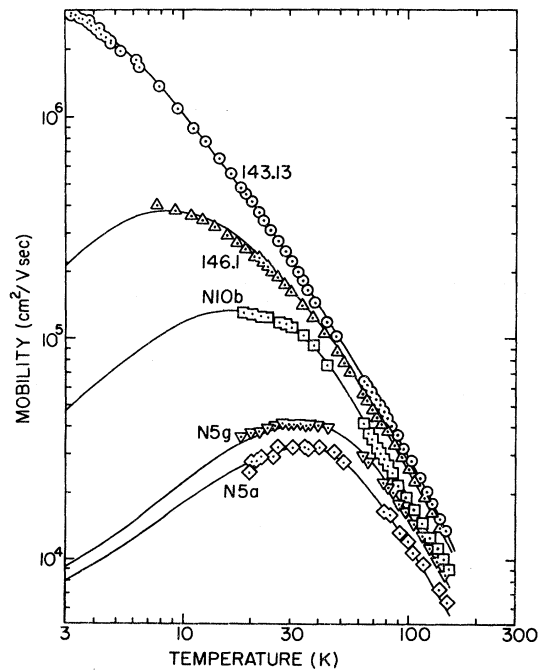The scale factor A used to modify the neutral-impurity-scattering contribution needs some com-

FIG. 2. Mobility as a function of temperature for five representative samples. Points show the experimental data; lines are drawn to show the calculated mobility using the parameters determined in the fitting program. Samples 143.13 and 146.1 show data taken from both Hall and photo-Hall measurements (Ref. 25).

TABLE I. Sample summary with results of mobility and carrier-concentration analysis for a one-acceptor model.

Sample number	Dopant	Diffusion temperature (°C)	N_d before diffusion (cm⁻³)	N_d from Hall-data analysis (cm⁻³)	N_d from mobility analysis (cm⁻³)	N_a from Hall-data analysis (cm⁻³)	Activation energy from Hall analysis (meV)	Degeneracy	A	G	Std. deviation of Hall fit
143.13	Cu	...	...	4.3×10^{10}	4.2×10^{10}	2.1×10^{13}	42.3	4.0	6.0[b]	1.11	0.42×10^{-2}
143.1P[a]	Cu	...	...	5.8×10^{10}	...	1.8×10^{13}	42.3	4.0	...	...	...
145.1	Cu	...	...	1.8×10^{11}	2.0×10^{11}	2.7×10^{13}	41.1	5.5	6.0[b]	1.17	0.78×10^{-2}
146.1	Cu	...	...	2.4×10^{12}	2.6×10^{12}	5.9×10^{13}	42.8	3.5	6.0[b]	0.99	0.34×10^{-2}
N5a	Cu:Sb	800	3.5×10^{14}	2.8×10^{14}	2.1×10^{14}	1.5×10^{16}	40.6	4.9	6.1	0.97	1.88×10^{-2}
N5e	Cu:Sb	800	9.0×10^{15}	8.1×10^{15}	4.8×10^{15}	1.9×10^{16}	37.7	6.0	3.6	1.04	1.63×10^{-2}
N5g	Cu:Sb	700	1.7×10^{14}	2.5×10^{14}	1.9×10^{14}	3.0×10^{15}	41.0	4.7	2.2	1.01	0.55×10^{-2}
N5h	Cu:Sb	800	1.3×10^{14}	1.5×10^{14}	1.5×10^{14}	1.7×10^{16}	40.4	5.1	6.7	1.03	0.78×10^{-2}
N10a	Cu:Sb	800	1.5×10^{13}	4.6×10^{13}	4.6×10^{13}	2.1×10^{16}	38.4	8.4	6.4	1.05	1.74×10^{-2}
N10b	Cu:Sb	675	1.5×10^{13}	1.7×10^{13}	1.8×10^{13}	2.2×10^{15}	41.5	4.2	5.0	1.09	0.50×10^{-2}
N11g	Cu:Sb	800	1.4×10^{15}	2.7×10^{15}	1.0×10^{15}	1.5×10^{16}	31.8	7.8	13.0	0.94	3.83×10^{-2}
N11i	Cu:Sb	800	1.3×10^{15}	7.1×10^{14}	6.7×10^{14}	1.5×10^{16}	36.6	9.0	6.8	1.00	0.75×10^{-2}
N12h	Cu:Sb	700	...	1.1×10^{14}	1.1×10^{14}	2.5×10^{15}	38.8	7.1	4.5	1.00	0.95×10^{-2}
RL174c[c]	Cu:As	700	9.9×10^{12}	2.1×10^{13}	1.3×10^{13}	4.1×10^{15}	30.4	47.0	4.4	1.09	3.55×10^{-2}
RL174b	Cu:As	700	9.9×10^{12}	3.9×10^{13}	1.1×10^{13}	3.8×10^{15}	33.6	20.0	5.3	1.04	2.97×10^{-2}

[a]Measurements of J. Stannard (unpublished).   [b]Value fixed.   [c]Sample RL174 was obtained through the generosity of R. N. Hall of GE.

TABLE II. Results of analysis for a two-acceptor model.

Sample	N_d from Hall-data analysis (cm⁻³)	N_a for copper (cm⁻³)	Activation energy of copper (meV)	Degeneracy of copper	N_a unknown impurity (cm⁻³)	Activation energy of unknown (meV)	Degeneracy of unknown	Std. deviation of fit
N10a	2.5×10^{13}	1.7×10^{16}	41.4	4.0[a]	1.1×10^{14}	32.6	4.1	0.94×10^{-2}
N10a	2.5×10^{13}	1.7×10^{16}	41.6	3.9	5.9×10^{13}	32.1	2.4	0.96×10^{-2}
N11g	1.5×10^{15}	1.0×10^{16}	38.2	4.7	2.8×10^{15}	30.1	4.0[a]	2.55×10^{-2}[b]
N11g	1.1×10^{15}	9.3×10^{15}	36.8	3.6	7.5×10^{15}	29.0	6.1	1.04×10^{-2}[b]
N11g	1.3×10^{15}	1.2×10^{16}	34.8	5.4	4.2×10^{16}	27.1	>100	0.88×10^{-2}[b]
N11i	7.1×10^{14}	1.4×10^{16}	36.6	8.6	9.1×10^{14}	36.4	8.7	0.82×10^{-2}[b]
N12h	1.2×10^{14}	2.3×10^{15}	40.0	6.3	1.9×10^{14}	35.9	2.8	0.73×10^{-2}[b]
N12h	1.2×10^{14}	2.4×10^{15}	38.6	6.9	1.6×10^{14}	38.4	7.0	0.57×10^{-2}[b]
RL174a	7.1×10^{12}	2.3×10^{15}	41.0[a]	4.0[a]	1.1×10^{14}	30.2	4.0[a]	0.96×10^{-2}
RL174a	1.0×10^{13}	2.4×10^{15}	41.0[a]	4.0[a]	4.8×10^{13}	30.2	1.0	0.80×10^{-2}
RL174a	9.2×10^{12}	2.3×10^{15}	42.2	4.0[a]	2.0×10^{14}	30.4	4.9	0.49×10^{-2}[b]
RL174a	7.6×10^{12}	2.4×10^{15}	40.1	6.0	1.4×10^{14}	30.1	5.2	0.37×10^{-2}
RL174b	1.1×10^{13}	2.8×10^{15}	41.0[a]	4.0[a]	1.3×10^{13}	27.6	4.0[a]	0.61×10^{-2}
RL174b	8.7×10^{12}	3.0×10^{15}	40.6	4.6	9.6×10^{12}	24.7	2.0	0.29×10^{-2}[b]
RL174b	8.6×10^{12}	3.0×10^{15}	40.6	4.6	9.5×10^{12}	24.7	2.1	0.29×10^{-2}

[a]Value fixed.   [b]Did not converge in 40 iterations.

TABLE III. The effect of varying parameters A and G on the determination of N_d by mobility analysis.

Sample number	N_d from mobility analysis (cm^{-3})	A	G	Std. deviation of mobility fit
143.13	4.2×10^{10}	6.0^a	1.11	2.3×10^{-2}
	4.0×10^{10}	4.0^a	1.11	2.2×10^{-2}
	3.4×10^{10}	2.0^a	1.11	2.2×10^{-2}
	2.8×10^{10}	6.0^a	1.00^a	9.1×10^{-2}
	3.4×10^{10}	6.0^a	1.05^a	5.2×10^{-2}
145.1	2.0×10^{11}	6.0^a	1.17	2.9×10^{-2}
	1.9×10^{11}	3.0^a	1.17	3.0×10^{-2}
146.1	2.6×10^{12}	6.0^a	0.99	4.1×10^{-2}
	2.5×10^{12}	3.0^a	0.99	4.0×10^{-2}
N5a	2.1×10^{14}	6.1	0.97	2.0×10^{-2}
	1.3×10^{14}	4.0^a	0.97^a	3.6×10^{-2}
	2.3×10^{14}	6.1^a	1.00^a	2.9×10^{-2}
N5e	4.8×10^{15}	3.6	1.04	1.2×10^{-2}
	5.3×10^{15}	6.0^a	1.04^a	1.4×10^{-2}
	4.5×10^{15}	3.6^a	1.00^a	1.1×10^{-2}
N5g	1.9×10^{14}	2.2	1.01	3.3×10^{-2}
	2.2×10^{14}	4.0^a	1.00^a	3.4×10^{-2}
	2.4×10^{14}	6.0^a	1.00^a	4.0×10^{-2}
N10b	1.8×10^{13}	5.0	1.09	3.0×10^{-2}
	1.1×10^{13}	5.0^a	1.00	7.2×10^{-2}
N11g	1.0×10^{15}	13.0	0.94	11.3×10^{-2}
	0.7×10^{15}	6.0^a	0.94	11.5×10^{-2}

^{a}Value fixed.

ment. The value should be unity for a hydrogenic impurity. In samples where neutral-impurity scattering was largest (N_a about 1.5×10^{16} cm^{-3}), the value of A was near 6, while at slightly lower concentrations (N_a about 3×10^{15} cm^{-3}), the average value was 4. This value could not be confirmed at lower acceptor concentrations, since the fitting program did not give realistic values of A in the purer samples. Often A would either become unreasonably large or small. This is because the purest samples are almost totally dominated by lattice scattering, and the lattice parameters did not give complete agreement with experiment. The computer apparently tried to adjust A to compensate for this discrepancy. We found that with the lattice parameters given by Brown and Bray we could not match our experimental mobility at both 77 and 150 K. This could be due to inaccurate thermometry above 100 K which is based on the copper-constantan thermocouple. Our solution was to fix the value of A and use only mobility data below 77 K in fitting the purest samples. For samples in the 140 series, we found that an adjustment of the value of A by a factor of 2 gave no appreciable change in the determination of N_d. This is because neutral scattering is very weak in these three purest samples.

In Table III we have attempted to show the influence of the factors A and G on the determination of N_d from the mobility analysis. Selected samples were refit with the parameters A and G fixed, but N_d allowed to vary. In the purest sample, 143.13, A could be varied by a factor of 3, while G could only be altered by 5% to produce similar changes in N_d. The standard deviation of the fit showed much stronger sensitivity to changes in G than in A. This is expected, since lattice scattering was dominant over much of the temperature range. Sample N5a, with less than 2% compensation and 1.5×10^{16}-cm^{-3} neutral-scattering centers at low temperatures, showed strong sensitivity to the choice of A. In this case, neutral-impurity scattering was more important than lattice scattering over a large portion of the temperature range. Not all of the more heavily doped samples showed significant variations in the value of N_d or the standard deviation as A was changed. Samples N5g, N5e, and N11g all had values of A that were as much as a factor of 2 from the average when the fits were made. Table III shows that none of these samples is particularly sensitive to the choice of A. In view of this, it is not likely that the fitted value of A will be very reliable for any one sample. We will, however, in Sec. V, attempt to understand why the average values lie in the range between 4 and 6.

The usefulness of the factor G can be illustrated by comparing the mobilities of the three purest samples at 77 K. Since at this temperature there should be very little impurity-scattering contribution, the true mobility should be equal for samples 143.13, 145.1, and 146.1. The measured mobilities were 4.68, 4.81, and 4.16×10^4 cm^2/V sec, respectively. Dividing these by the value of G obtained in each case from the curve-fitting procedure, the corrected mobility values are 4.22, 4.12, and 4.20×10^4 cm^2/V sec for samples 143.13, 145.1, and 146.1. This agreement, which is within the limits of experimental uncertainty, gives us some assurance that G was reasonably fit in these three cases.

Another remark should be made on these three purest samples. We originally ran the mobility program using only data from 20-77 K. Although sample 146.1 gave a fairly good fit, samples 145.1 and 143.13 fit with unreasonably low values of N_d. This only indicates that ionized-impurity scattering is very weak in these samples. Because of this difficulty, we made a trial fit using both Hall and photo-Hall data.[25] Some caution is required when data below 20 K are fit to the ionized-impurity-scattering formula given by Brooks, Herring, and Dingle, since it is possible to violate the Born approximation in which this formula is derived. We must have $|ka| \gg 1$, where $\vec{k}$ is the carrier momentum, and a is the scattering length,[20] to be in the
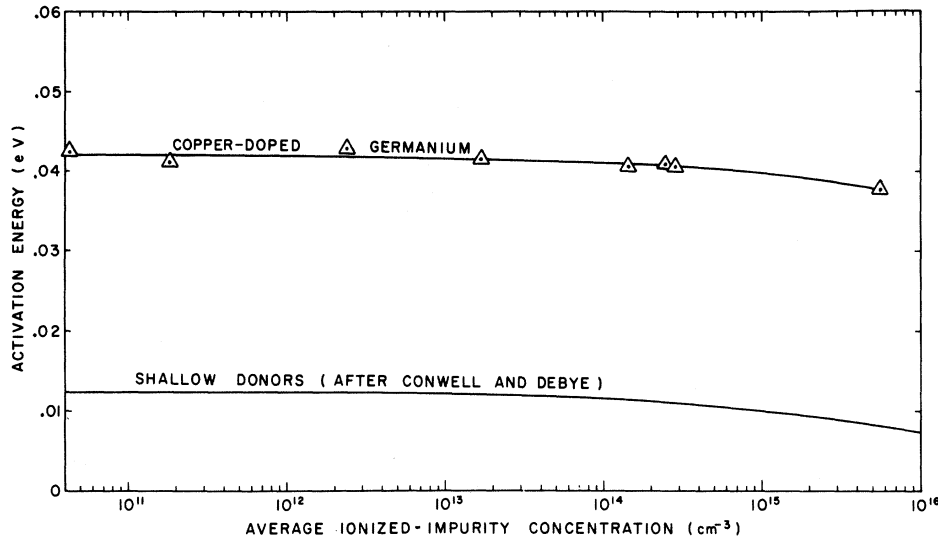
FIG. 3. Activation energy of copper-doped germanium as a function of the average ionized-impurity concentration. For comparison, the results for shallow donors in germanium are included (Ref. 1). The solid line through the data shows the fit of the empirical formula described in the text. Parameters determined from this fit did not change when the single datum point representing sample N5e (compensation about 6×10^{15} cm^{-3}) was omitted, even though it may appear to be singularly influential in the figure.

range of validity. For germanium we find $|\vec{k}a|$ $= 1.5 \times 10^7 T(m^*/p_s)^{1/2}$, where $p_s = p + (p + N_d)[1 - (p + N_d)/N_a]$. Using the light-hole mass of $0.045m_0$, we find $|\vec{k}a|$ equal to $15T$, $7.5T$, and $2.1T$ for 143.13, 145.1, and 146.1, respectively. Data were used down to 3 K for 143.13, down to 4 K for 145.1, and down to 7 K for 146.1. Tables I and III show the results of using both Hall and photo-Hall mobility data for making this fit. Agreement is very good with the values of N_d obtained from carrier-concentration data, and can be seen to be quite independent of the choice of A. Consequently, we feel justified in using these combined data. It is also good evidence that the photoexcited holes were in thermal equilibrium with the lattice in this same temperature range.

V. COMPARISON WITH OTHER EXPERIMENTS

The activation energy of copper-doped germanium is shown in Fig. 3 as a function of the average ionized-impurity concentration. Also shown are the results of similar measurements made on shallow donors.[1] As can be seen, the activation energy decreases with increasing ion concentration. We fit the experimental points to the empirical formula

$$E_a = E_a(0) - \alpha N_i^{1/3} , \tag{2}$$

where N_i is the average number of ionized impurities in the freeze-out region. The value of $E_a(0)$ was found to be 0.0422 eV, which can be compared with the optical activation energy of 0.04286 eV. The value of α was found to be 2.4×10^{-8}, and is in agreement with the value reported for shallow donors, 2.35×10^{-8}. It is interesting that the value of α appears to be independent of the impurity binding energy. This implies that the decrease in acti-

vation energy with increasing ion concentration occurs due to a disruption of the band states rather than the impurity states. Data used in this analysis were selected from those samples which did not show unusual activation energies when analyzed with the program for a single acceptor level.

The three purest crystals (143, 145, and 146) should give the most reliable value of the degeneracy, since the high-temperature exhaustion region was reached in the range of temperatures measured. For these samples, the degeneracy is about 4. This is in agreement with the theoretical prediction for a shallow acceptor state. According to the formulation of Kohn,[26] the equation for the impurity problem is

$$H_0 \psi(\vec{r}) + U(\vec{r}) \psi(\vec{r}) = E\psi(\vec{r}) , \tag{3}$$

where H_0 is the Hamiltonian of the hole in the crystal, and $U(\vec{r})$ is the potential of the impurity ion. The solutions for H_0 alone will be the Bloch functions. For shallow acceptors, $U(\vec{r})$ is chosen to be $-e^2/\kappa r$. However, the degeneracy of 4 arises because the solution is found using H_0 for the upper two valence bands alone, neglecting the split-off band. This approximation is made because the spin-orbit splitting is much larger than the acceptor binding energy. Since this same approximation is valid for the first acceptor level of copper, we may ask how the solutions will differ from those found for shallow acceptors. At large distances the potentials will be identical, as evidenced by the agreement of excited-state energy spacing.[27,28] Because copper binds two additional holes, however, we should have to take hole-hole interaction potentials into account. This may not be overly important. The two bound holes on the singly ionized copper impurity are bound very tightly

and if any analogy to atomic lithium were applicable, they would be in a $1S^2$ subshell. Considering then the singly ionized copper impurity as a spherically symmetric potential, stronger at the core than a shallow acceptor, we find that the degeneracy should be the same as for the shallow acceptor. This is because the form of the solution will not depend on the exact radial function of $U(\vec{r})$. A group-II impurity in germanium could be expected to have some additional complications due to the strong hole-hole interactions. In fact, the ground-state energy levels of mercury show splitting, as evidenced in the excited-state transition spectra.[29]

Degeneracies of 2 for gold and nickel were reported by Ostroborodova,[30,31] while a value of 8 for gold was found by Klein and Debye.[32] Since both of these measurements rely on Hall-factor corrections in the temperature range above 100 K, the results on these considerably deeper levels are difficult to compare with our result for copper.

Approximate calculations of mobility given in many other papers have shown fair agreement with experiment. We have shown that a more exact treatment of the averaging process (i.e., numerical integration) gives very good results. A large part of this success must be attributed to the accuracy of the Brooks-Herring-Dingle formula for ionized-impurity scattering. Long and Myers[33] have found consistency with this formula for mobility in silicon. Our success with the Brooks-Herring-Dingle formula is in contrast to a recent paper by Cuevas,[34] who finds that the theory does not provide agreement over the entire range and suggests an alternative theory. The main difficulty observed by Cuevas was an increase in the ionized-impurity mobility, as the density of neutral impurities increased, which exceeded the increase predicted by the Brooks-Herring-Dingle formula. This disagreement may possibly be reconciled by a correction to the neutral-scattering contribution. The Erginsoy formula is derived for the case of an electron scattering from a single, neutral, hydrogenic impurity. However, for neutral-impurity concentrations above 10^{15} cm^{-3}, the de Broglie wavelength of the carrier becomes comparable to the interimpurity spacing, and coherent scattering involving more than one impurity becomes important. In p-type germanium, the heavy-hole wavelength is about 500 Å at 25 K, and the most probable impurity pair separation is about half that value for a concentration of 10^{16} cm^{-3}. For copper-doped germanium, with N_a about 1.5 $\times 10^{16}$/cm^{-3}, we find the average scattering time is a factor of 6 longer than predicted by the hydrogenic model. When N_a is about 3×10^{15} cm^{-3}, we find an average correction factor of only 4. Electron-scattering measurements by Otsuka, Murase,

and Takesawa[35] also show that the scattering time for neutral scattering by copper is less than a simple N_a^{-1} dependence in the same range of N_a. Similar conclusions have been reached by Honig and Maxwell[36] for neutral scattering in silicon. Such an effect for shallow impurities may explain the lack of agreement found by Cuevas, since a decrease in the neutral-impurity-scattering effectiveness at high concentrations would give a mobility enhancement as the concentration of neutral centers increased.

The question of how to scale the Erginsoy equation for deep acceptors is not obvious. Erginsoy formulated the neutral-scattering time in terms of the scaled Bohr radius: $1/\tau = 20a_0\hbar N_N/m^*$; and this makes it tempting to use a readjusted radius to correct for the difference in binding energy between a hydrogenic and deep acceptor. Using the quantum-defect method, the radius of copper should be about half the radius of a shallow level, so that the scattering time would be twice as long. This analysis is questionable however, in view of the partial-wave-technique formulation underlying Erginsoy's expression. Since only the zero-order phase shift is used, the problem is mathematically similar to low-energy scattering from a hard sphere or any other finite-range potential in the limit $|\vec{k}a| \ll 1$ and $a \ll \lambda$, where λ is the de Broglie wavelength of the carrier. If we assume the scattering length to be proportional to the scaled Bohr radius, then the scattering cross section depends on the square of the radius. This gives a correction factor of 4 to the neutral-scattering time for copper, in agreement with the average experimental result for N_a of about 3×10^{15} cm^{-3}.

VI. CONCLUSION

We have shown that very good agreement can be obtained between carrier-concentration and mobility analysis for determining the compensation density in copper-doped germanium. With similar care, modifying the contributions due to neutral-impurity scattering, mobility analysis of other nonhydrogenic impurities in germanium can be used to determine compensation levels. Our analysis of this series of copper-doped samples will be the basis for further papers on the transport and recombination properties in these samples.

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