Electrical conductivity of germanium as a function of optically injected carrier density and temperature

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The effects of carrier-carrier scattering on the transport properties of high-density electron-hole plasmas in germanium were studied both experimentally and theoretically. Experimentally, the dc electrical conductivities of nearly uniform optically injected bipolar plasmas in high-purity single crystals of germanium were measured for a broad range of carrier densities ($\sim 10^{14}$–$\sim 5\times10^{17}$ cm^{-3}) and temperatures (21–298 K). Concurrent measurements of the absorption of 3.39-μm radiation due to inter-hole-band transitions aided the calibration of the carrier densities at some temperatures. The previous theory of Appel, which used Kohler's variational principle to solve the Boltzmann equation, was generalized with respect to the inclusion of interband hole scattering, electron mass anisotropy, degeneracy, and use of the RPA $\vec{q}$-dependent screening approximation (although not with respect to all at once). The most crucial generalization was the accounting for the presence of nonconducting excitons in the plasma. The scattering of free carriers by excitons was also considered, using a neutral-impurity scattering theory similar to that of Erginsoy. Incorporation of all the above considerations led to excellent agreement between experiment and theory at densities below the Mott criterion for transition to the exciton-free phase. The transition itself appeared to be gradual, however, and behavior of the conductivity in the high-density region was consistent with the recent assertion by Thomas and Rice that excitons are present at densities significantly above the Mott criterion.

I. INTRODUCTION

The effect of carrier-carrier scattering on the electrical transport properties of uniform bipolar plasmas in germanium has been investigated both experimentally and theoretically for a broad range of carrier densities ($\sim 10^{14}$ cm^{-3}–$\sim 5\times10^{17}$ cm^{-3}) and temperatures (21–298 K). Despite the very fundamental nature of the problem, it has received surprisingly little previous experimental attention. (Although many photoconductivity experiments have been reported, very seldom has an attempt been made to determine the conductivity as a function of uniform carrier density such that results could be compared with theories which incorporate carrier-carrier scattering effects.) Data for Ge (Ref. 1) and Si (Ref. 2) at 300 K, for Ge (Refs. 3–5) and Si (Ref. 6) at 4 K and below, and Te (Ref. 7) at 77 and 4 K, have been reported concerning the transport properties of bipolar plasmas. (None of the germanium results is directly comparable to the present experiment.) Additional experiments have been reported concerning the effect of carrier-carrier scattering on the transport properties of unipolar plasmas[8] in Ge at 77 K and on the mobility of minority carriers[9] in doped Ge at temperatures between 20 and 160 K. It must be concluded, however, that the work cited is of insufficient range and sensitivity to offer a critical test of relevant transport theories, especially in the temperature region 21–298 K which was studied in the present experiment. (Due to the high degeneracy and to the presence under certain conditions of electron-hole droplets, the very-low-temperature region is qualitatively quite different from that studied here.)

The previous theory which is most applicable to the present problem is that of Appel,[10] in which he used Kohler's variational principle[11] to solve the simultaneous electron, heavy-hole, and light-hole Boltzmann equations while accounting for carrier-carrier interactions as one of the scattering mechanisms. Comparison with the present experimental results shows, however, that Appel's theory almost always overestimates the conductivity. For this reason, the theory has been made more general in a number of ways (but not with respect to all of the following simultaneously):

(i) Whereas Appel treated only intraband processes, that is, processes in which all carriers are required to remain in the same band throughout the interactions, the theory has been generalized to include interband hole transitions. (An example is an event in which a heavy hole and a light hole enter an interaction, but two heavy holes come out.)

(ii) Instead of using Boltzmann statistics, results have been obtained for arbitrary degeneracy.

(iii) Whereas the previous calculation assumed isotropic masses, the anisotropy of the electron

valleys has been taken into account.

(iv) The random-phase approximation (RPA) screening approximation, which is wave-vector and degeneracy dependent, has been employed instead of Debye-Hückel screening.

While the above generalizations affect the conductivity by nearly a factor of 2 in some regions, it is shown that the necessity of accounting for the presence of excitons is also important. After deriving the expected number of excitons from the assumption of thermal equilibrium between excitons and free carriers, the conductivity due only to the free carriers was determined. The importance of exciton scattering has also been estimated using scattering cross sections derived from an extension of the neutral-impurity mobility theory of Erginsoy.[12] The range of validity of that theory has been clarified.

It will be seen that excellent agreement between experiment and theory is obtained for densities below the Mott criterion[13] for transition to the metallic (exciton-free) phase, while above the transition density the experimental conductivity is slow in joining the exciton-free theory. Such behavior is consistent with the recent assertion by Thomas and Rice[14] that there is no sudden metal-insulator transition, but rather that the bound state is still present at densities significantly above the Mott criterion.

II. EXPERIMENTAL ARRANGEMENT

Measurements were made on five different single-crystal slabs of germanium with initial impurity density $\sim 5 \times 10^{10}$ cm^{-3} (p type). The samples were approximately 6 mm long, 3 mm wide, and 170 to 380 μm thick. Metal dots of diameter ~100 μm were alloyed into the edges at ~400 °C in order to make electrical contact. Three to five dots of indium containing 0.5% gallium (which makes a p^+ region within the germanium) and of tin containing 3% antimony (which makes an n^+ region) were alloyed into each end in order that both electrons and holes could readily pass into and out of the crystals. Two additional dots alloyed into each long edge allowed four-probe measurements of the conductivity. Samples were mechanically polished to thickness with 1-μm and 0.3-μm alumina and given a final etch in CP-4A (25 parts HNO_3, 15 parts HF, and 15 parts glacial acetic acid). They were then mounted at one end such that both faces could be illuminated by the incident excitation radiation.

Excitation was provided by 1.06-μm radiation from a Holobeam Series 300 laser which contained a Nd-glass rod. Pulses of 30-nsec duration were produced using a Pockels Cell Q switch. The beam was attenuated by a series of calibrated reflection and absorption filters, after which it was split and directed toward opposite faces of the sample. Ground-glass diffusers were placed in the path near the sample in order to help average out any lateral nonuniformity of the radiation. The intensity profile was roughly Gaussian with half-width ~6 mm, which was large enough to cover the sample.

In order to aid the calibration of the carrier densities, the absorption of 3.39-μm radiation from a He-Ne laser was determined along with the conductivity. The intensity of the transmitted 3.39-μm beam was measured with a liquid-nitrogen-cooled InSb photoconductive detector (rise time ~0.1 μsec). The samples were sufficiently wedge shaped that Fabry-Perot effects were not significant. Measurements were made inside a Janis 8DT "Super-Vari-Temp" Dewar with sapphire windows. Cooling was provided by exchange gas from the liquid-helium reservoir and temperatures were determined with a Chromel vs Au–0.07-at.%-Fe thermocouple which was in good thermal contact with the sample.

The conductivity and absorption (of 3.39-μm radiation) measurements were made simultaneously 1.5–4 μsec after the excitation pulse, which was sufficient time for the injected carriers to have diffused throughout the sample. An analysis of the diffusion problem using the observed lifetimes of 4–15 μsec (which were due primarily to surface recombination) shows that under most circumstances the injected plasmas should have been quite uniform.[15] Unfortunately, in the region at low temperatures where it will be seen that carrier-carrier scattering has the effect of decreasing the mobilities by an order of magnitude or more from the low-density values, it must be concluded that the uniformity was not particularly good in some samples (whereas it should always have been good in others). It must be remembered that a lack of uniformity has an effect on the measured result proportional only to the second derivative of the conductivity with respect to density. Since, as will be seen, the results agreed well from sample to sample, it is asserted that nonuniformity did not have a large effect on the values measured for the conductivity.

III. EXPERIMENTAL RESULTS

The experiment was performed at seven different temperatures: 298, 215, 124, 72, 48, 32, and 21 K. At the higher temperatures (124 K and above) the measurements of the absorption of 3.39-μm radiation were used to calibrate the carrier densities. The absorption in Ge at this wavelength is

primarily due to transitions between the heavy-hole band and the split-off valence band.[16] Because of the different curvatures of the two bands, the photon energy required for a particular vertical transition depends on the location in k space. Thus, if higher-order processes are ignored, the absorption coefficient should be proportional to the number of holes present in the heavy-hole band at the location appropriate for a photon of energy corresponding to the wavelength 3.39-μm. (At the densities and temperatures studied, degeneracy considerations do not greatly affect this assumption, although they would at sufficiently high density.) It is thus possible to derive the density of holes p from the absorption coefficient α if the cross section for absorption of a single hole σ_C is known for the proper wavelength

$$p = \alpha(3.39\ \mu\text{m})/\sigma_C(3.39\ \mu\text{m}). \quad (1)$$

Pinson and Bray measured the infrared absorption as a function of photon energy for p-type germanium doped to a known hole density at a number of temperatures between 77 and 296 K.[16] The 3.39-μm cross sections listed in the Appendix for the temperatures of interest were estimated from their data.

Figure 1 shows the absorption results for a particular sample at 298 K. The quantity plotted has been "normalized"

$$\bar{\alpha} = A\alpha/I, \quad (2)$$

where α is the measured absorption (cm^{-1}), I is the intensity of the excitation, and A is a normalization constant which was chosen so that the value of $\bar{\alpha}$ is unity at low I. With this definition of $\bar{\alpha}$, a flat line of magnitude unity would have been obtained had the absorption always been proportional to the density and the density always proportional to I. Apart from random fluctuations, such behavior is indeed evident at the lower excitation levels. Also apparent, however, is a striking decrease in $\bar{\alpha}$ at large I. This is believed to be due to Auger recombination at the faces of the sample immediately after excitation. It must be remembered that the absorption length of 1.06-μm wavelength radiation in Ge is ~1-μm whereas the samples were ~200-μm thick. Thus, in order to obtain an average density n of 5×10^{17} cm^{-3}, an initial density of at least 5×10^{19} cm^{-3} had to be injected into the first micrometer of each face. Because Auger recombination is proportional to n^3 it is not surprising that the final densities were affected by a significant amount under such conditions.

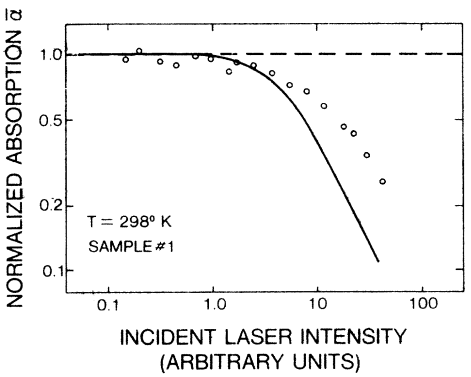

FIG. 1. Normalized absorption $\bar{\alpha}$ of sample 1 at 298 K. The solid curve predicts the effect of Auger recombination.

Whereas the inclusion of Auger recombination into the full diffusion equation would render it too complex to be solved analytically, a simple calculation using a rather crude model has been carried out.[15] The values (for 298 K) $\gamma = 1.1\times10^{-31}$ cm^6/sec,[17] $\alpha^{-1}(1.06\ \mu\text{m}) = 1.2\ \mu\text{m}$,[18] and $D = 71.1$ cm^2/sec were used, where γ is the Auger rate constant, α^{-1} the absorption length of 1.06-μm radiation, and D the ambipolar diffusion constant (based on the electron and hole mobilities listed in the Appendix). The result of the calculation, shown as the solid curve of Fig. 1, agrees well enough with the experiment to leave little doubt that Auger recombination was indeed responsible for the decrease in $\bar{\alpha}$ at high densities. At temperatures below 298 K, the Auger rate constant has not been well established experimentally. The present data indicate that it decreases with decreasing temperature down to 124 K. (As will be discussed below, the absorption measurements below that temperature were less reliable.)

With the measured absorptions along with the cross sections approximated from Ref. 16 (which are given in the Appendix), Eq. (1) has been used at temperatures 124 K and above to calibrate the carrier density corresponding to each conductivity measurement. At injection levels too low for the absorption signal to be measured, a linear relationship has been assumed between carrier density and laser intensity. The flatness of $\bar{\alpha}$ at low I appears to justify this assumption.

For the conductivity as a function of carrier density at 298, 215, and 124 K, this density-calibration procedure yields the experimental points of Figs. 2(a)–2(c), the quantity plotted (mobility ratio) has again been normalized:

$$\sigma/\sigma_0 = \sigma/ne(\mu_{e0} + \mu_{h0}), \quad (3)$$

where σ is the measured conductivity, n is the density found as described above, and μ_{e0} and μ_{h0} are the low-density electron and hole phonon mo-

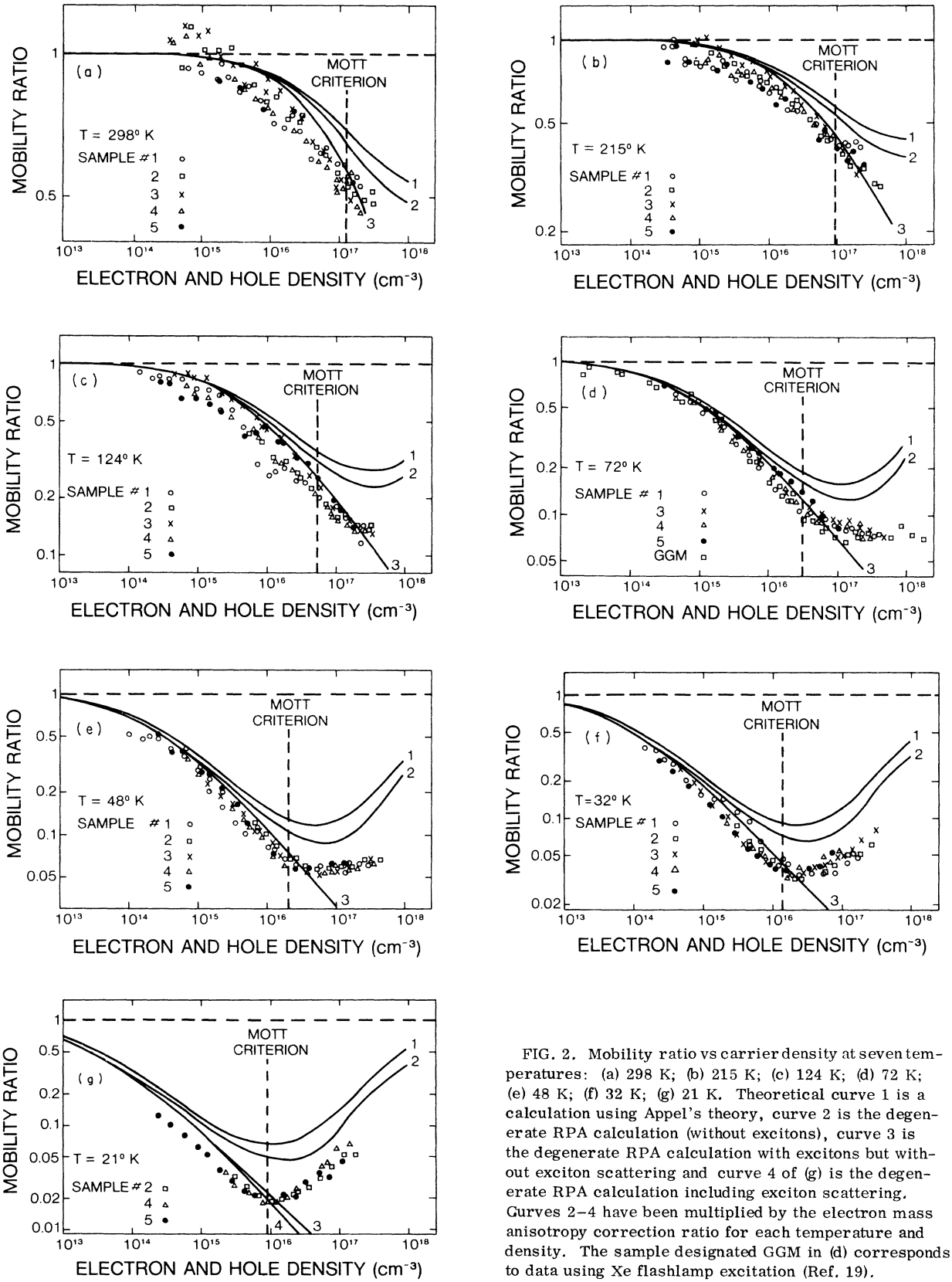

FIG. 2. Mobility ratio vs carrier density at seven temperatures: (a) 298 K; (b) 215 K; (c) 124 K; (d) 72 K; (e) 48 K; (f) 32 K; (g) 21 K. Theoretical curve 1 is a calculation using Appel's theory, curve 2 is the degenerate RPA calculation (without excitons), curve 3 is the degenerate RPA calculation with excitons but without exciton scattering and curve 4 of (g) is the degenerate RPA calculation including exciton scattering. Curves 2–4 have been multiplied by the electron mass anisotropy correction ratio for each temperature and density. The sample designated GGM in (d) corresponds to data using Xe flashlamp excitation (Ref. 19).

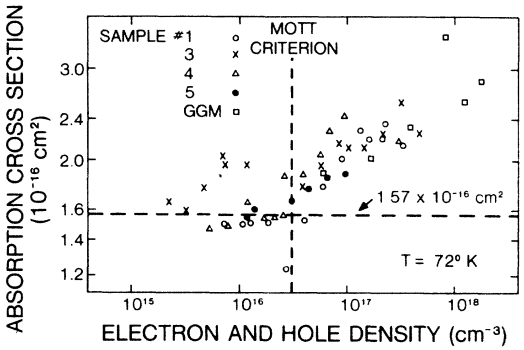

FIG. 3. Absorption cross section of 3.39-μm radiation at 72 K. The value 1.57×10^{-16} cm^2 was extrapolated from the data of Pinson and Bray. GGM refers to data using Xe flashlamp excitation (Ref. 19).

bilities determined experimentally by others. (The Appendix lists the values used at the different temperatures.) The significance of the various theoretical curves will be explained in Sec. IV.

At temperatures below 124 K, the density calibration was less straightforward. For example, the absorption data at 72 K are shown in Fig. 3. Here the quantity plotted is the cross section one obtains using Eq. (1) with densities obtained from the conductivity data (in a manner which will be described below.) The low-density cross sections for samples 1, 4, and 5 approximate well the value $\sigma_c=1.57\times10^{-16}$ cm^2 which was extrapolated from the data of Pinson and Bray.[16] However, a marked increase is noted at the higher densities, which could be due to multiparticle-absorption processes. While the qualitative behavior was similar at 48 K and below, the cross sections obtained at those temperatures showed poor agreement from sample to sample, although the conductivity data were no less consistent than at the higher temperatures.

Figure 2(d) shows the conductivity data at 72 K. The calibration of the carrier densities is based on the fit between theory and experiment at low densities and on the assumption that the injected density was linear with the intensity of the excitation laser. Since the same calibration also gives good agreement between the absorption cross section measured at low densities and that extrapolated from the data of Pinson and Bray, the carrier-density calibration at this temperature is relatively unambiguous. The assumption of linearity is supported by the excellent agreement between the present experiment and that reported previously,[19] [designated GGM in Figs. 2(d) and 3] which was similar except that Xe flashlamps were used for excitation and only one temperature, 72 K, was studied. Because the excitation pulse in that experiment lasted ~3 μsec, Auger recombination should not have been a factor. It is argued that a nonlinearity of injection level present for one of the excitation systems should not have been repeated for the other, quite dissimilar system.

The density calibrations for 48 K and below were based primarily on the assumption that the quantum efficiency of the injection did not change as a function of temperature. That is, whatever density was assumed for a particular laser intensity at 72 K was also assumed for the same intensity at the other temperatures. Occasionally the calibration for a particular sample had to be shifted as the temperature was changed (probably because the alignment of the excitation system was slightly better or worse than it had been during the previous run) in order to keep the curve for that sample lined up with those for the others, but in general the good fit from sample to sample was maintained by assuming that the calibration was independent of temperature. With this assumption, the relation between the theoretical curves and the experiment seems to be consistent from temperature to temperature (except perhaps at 21 K).

Summarizing, it is unfortunate that no absolute calibration of the carrier densities is available at the lower temperatures. Based on all the considerations discussed above, however, it is asserted that the densities assumed in the plots are probably reasonably accurate over most of the range (within perhaps 15%). Above $\sim2\times10^{17}$ cm^{-3}, some of the experimental curves at the lower temperatures appear to bend down slightly in a manner contrary to what is expected (especially at 48 and 72 K). While this may, of course, be a real effect, it seems more likely that either Auger recombination has invalidated the assumption of linearity at the highest injection levels or that there was error in the measurement of the very-high-density conductivities (which are difficult to obtain accurately because of the very low resistances).

IV. COMPARISON OF THEORY AND EXPERIMENT

The theory of Appel,[10] in which he used Kohler's variational principle[11] to solve the simultaneous Boltzmann equations for the electron, heavy-hole, and light-hole bands, has been generalized with respect to the inclusion of interband hole scattering, degeneracy, electron mass anisotropy, and the use of the RPA dielectric constant to account for screening rather than the less general Debye-Hückel approximation. (The expressions were also made general with respect to the frequency dependence of the applied electric field, although the experiment involved only dc measurements.) Unfortunately, the detailed exposition of the theory is lengthy and tedious, and will thus not be given

here. The interested reader is referred to Ref. 15 for a full development of the results which will be summarized below. It should be noted that a consequence of implementing the various generalizations of the theory is that whereas Appel obtained expressions containing single integrals, the revised formulations contain twofold, fourfold, or fivefold integrals. The numerical evaluations were, however, carried out by computer to within better than 1%.

The variational principle provides a technique of solving the Boltzmann equation for a plasma of mobile charged particles which yields the electrical conductivity in the form of the ratio of the determinants of two matrices. Successive approximations are obtained by adding rows and columns to the matrices, each order giving a higher conductivity than the one before. Convergence is fortunately quite rapid for the present problem. Although the results which follow are based on zero- and first-order approximations, the authors found from sample cases involving higher orders that for the types of scattering being considered the first-order result varies no more than 5% (sometimes much less) from the infinite-order result. An extrapolation procedure was followed which yielded approximations of the infinite-order results which were probably accurate to within ~2%. A nearly exact solution of the Boltzmann equation (as it is formulated) is thus possible. Of course, the conductivity obtained will be accurate only to the extent to which all of the relevant scattering mechanisms have been included, the band-structure approximations and the forms of the scattering potentials are appropriate, and the Boltzmann equation itself is valid in the region of interest.

The results of Appel's calculation, extrapolated to infinite order, are shown as curves 1 of Fig. 2. (Nondegeneracy, isotropic masses, no interband hole scattering, Debye-Hückel screening, and the absence of excitons were assumed.) The high-density upturn of the mobility predicted for the lower temperatures occurs because after a certain critical density, the addition of carriers has a greater tendency to increase the mobility due to the increased effectiveness of the screening than it has to decrease it due to the presence of a larger number of scattering centers. It is evident that the experimental mobilities are always overestimated, often by large amounts.

In this and the other calculations which will be described below, the phonon scattering was all assumed to be due to acoustical phonons. Because optical phonons have different energy-redistributing properties, this simplification introduces error (probably no more than ~2% to 3%) at the higher temperatures (above ~80 K).[20] When interband

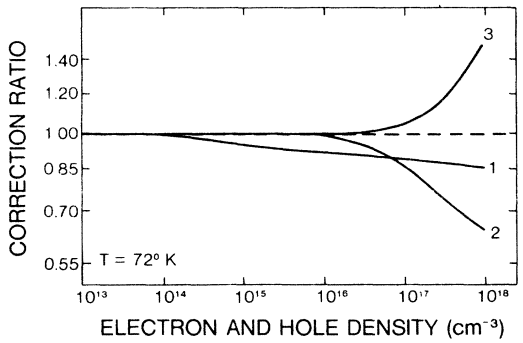

FIG. 4. Corrections to the conductivity due to the various theoretical improvements. Curve 1 is σ_0(anisotropy)/σ_0(Appel), curve 2 is σ_1(RPA-nondeg)/σ_1(Appel) and curve 3 is σ_1(RPA-deg)/σ_1(RPA-nondeg).

hole scattering (and proper coupling of the hole bands[21]) was included for nondegenerate statistics and Debye-Hückel screening, it was found that the correction to the conductivity obtained from Appel's results was everywhere less than 5% at the temperatures and densities of interest.

The inclusion of electron-mass anisotropy, on the other hand, reduced the calculated conductivity by as much as ~15%, as shown for 72 K by curve 1 of Fig. 4. The quantity plotted is the ratio of the zero-order anisotropic result to Appel's zero-order result. One reason for the decrease in conductivity is the increased importance of electron-electron scattering. Because of momentum conservation, electron-electron scattering has only a higher-order effect on the conductivity[22] when isotropic masses are assumed. Although the same is true of scattering between electrons in the same anisotropic valley, events between electrons in different anisotropic valleys limit the conductivity in zero order.

Curve 2 of Fig. 4 represents the ratio of the result of the calculation which employed the RPA screening approximation in first order (in the nondegenerate limit) to Appel's first-order result. The RPA dielectric constant was first derived by Lindhard[23] from perturbation theory, but takes its name from a more general rederivation using the random-phase approximation.[24] The following form was used for the screened Coulomb potential as a function of wave vector:

$$V(\vec{q}, \omega = 0) = 4\pi e^2/\kappa_0(q^2 + q^2_{\mathrm{RPA}}), \tag{4}$$

where κ_0 is the static dielectric constant and q_{RPA} is the zero-frequency inverse screening length in the RPA approximation, which may be written

$$q^2_{\mathrm{RPA}} = q^2_D \left(\frac{F_{-1/2}(\eta)}{F_{1/2}(\eta)}\right) G(\vec{q}, \eta), \tag{5}$$

where q_D is the Debye-Hückel result

$$q_D^2 = 4\pi n e^2/\kappa_0 k_B T , \tag{6}$$

n is the carrier density, F_k is the Fermi integral of order κ,[25] and η is the reduced Fermi energy ($=E_F/k_BT$).

The following limiting values may be obtained:

$$\lim_{q\to 0} G = 1,$$

$$\lim_{\eta\to-\infty} q_D^2 \left(\frac{F_{-1/2}}{F_{1/2}}\right) = q_D^2, \tag{7}$$

$$\lim_{\eta\to+\infty} q_D^2 \left(\frac{F_{-1/2}}{F_{1/2}}\right) = q_{TF}^2 = \frac{6\pi n e^2}{\kappa_0 \eta k_B T},$$

where q_{TF} is the Thomas-Fermi wave vector. As $|\vec{q}|$ increases, $G(\vec{q},\eta)$ monotonically decreases from unity, indicating that high-q screening is less effective than low-q screening. Although G may be found analytically in the extreme degenerate limit, it is reducible only to an integral with two independent parameters elsewhere. Ref. 15, however, gives analytic approximations of G valid for any q or η, which should simplify the use of the RPA result in regions where extreme degeneracy is not applicable. (Isotropic parabolic uncoupled bands were assumed.)

It can be seen from curve 2 of Fig. 4 that incorporation of the q dependence of the screening decreases the conductivity at 72 K by a significant factor at the higher densities. The decrease is even greater for lower temperatures.

Curve 3 of Fig. 4 represents the result of using Fermi rather than Boltzmann statistics. The RPA dielectric constant was also employed, this time using the evaluations which are general with respect to both wave vector and degree of degeneracy. In this case the quantity plotted is the ratio of the degenerate RPA calculation in first-order to the nondegenerate RPA result in the same order. The inclusion of degeneracy is seen to increase significantly the theoretical conductivity at the higher densities.

Curves 2 of Fig. 2 show the degenerate RPA result, extrapolated to infinite order and multiplied by the correction ratio for electron-mass anisotropy for each temperature and density. That is, it has been assumed that the correction due to the incorporation of anisotropy into the degenerate RPA calculation is probably similar to that due to its incorporation into the nondegenerate, constant screening calculation. Since the interband scattering had little effect in the nondegenerate, constant screening case, curves 2 of Fig. 2 are probably a good indication of the results one would obtain were all the generalizations incorporated at once.

The effects of allowing for the presence of excitons will now be considered. The relations

$$n_I = n_F + n_{ex} = n_F + n_{ex}^+ + n_{ex}^- , \tag{8}$$

and[26]

$$n_{ex}^{\pm} = n_F^2 \left(\frac{2\pi\hbar^2}{k_B T}\right)^{3/2} \left(\frac{(m_T^{\pm})^{2/3}(m_L^{\pm})^{1/3}}{m_e(m_h+m_l)}\right) e^{E_{ex}^{\pm}/k_B T} \tag{9}$$

allow the calculation of the density of free carriers n_F and excitons n_{ex} as functions of the total density of carriers injected n_I. In Eq. (9), which assumes thermal equilibrium between the excitons and free carriers, n_{ex}^+ and n_{ex}^- are the densities of the two doubly degenerate excitons of germanium while the $E_{ex}^{\pm}$ are the corresponding binding energies. $m_T^{\pm}$ and $m_L^{\pm}$ are the transverse and longitudinal masses of the excitons, m_e the density-of-states electron mass, and m_h and m_l the heavy- and light-hole masses. The exciton masses and binding energies given by Frova *et al.*[27] have been used.

Curves 3 of Fig. 2 represent the result of applying Eqs. (8) and (9) to the degenerate RPA result (again multiplied by the anisotropy-correction ratio). That is, whereas both the abscissa of Fig. 2 and the quantity n in Eq. (3) have been taken to be the injected density n_I, the conductivity σ of Eq. (3) has been recalculated using n_F for the carrier density. It is seen that the effect on the calculated conductivity is large, even at the highest temperatures. Implicit in the calculation of curves 3 are the assumptions that the excitons neither conduct nor scatter the free carriers. The latter of these assumptions will now be examined.

The scattering of free carriers by excitons in semiconductors has received little theoretical attention. Similarly, exciton scattering is difficult to isolate experimentally, although a cross section slightly smaller than that predicted by the neutral-impurity scattering theory of Erginsoy[12] was obtained by Ohyama, Sanada, and Otsuka[28] from measurements of the time-dependent linewidth of the cyclotron resonance of photoexcited electrons in Si at 4.2 K. As no clear-cut procedure for dealing with exciton scattering is available, the present results will also be compared with neutral-impurity scattering theory. The approach taken will be similar to that of Erginsoy,[12] in which he inserted the semiconductor static dielectric constant κ_0 into the low-energy results of Massey and Moiseiwitsch[29] for the elastic scattering of electrons from hydrogen atoms. He used the cross section

$$\sigma(k,\theta) = 20a_0^2/4\pi y^{1/2}, \qquad y \equiv (ka_0)^2 \tag{10}$$

where a_0 is the effective Bohr radius and the fac-

tor 20 is empirical.

While one obtains $ka_0 \approx 0.6$ for thermal-energy electrons at 21 K, the validity criterion, $ka_0 \ll 1$ is usually given in connection with Eq. (10). For this reason, the analysis which follows will employ the more general empirical cross section

$$\sigma(k,\theta) = \sigma_B(k,\vartheta)R(y), \tag{11}$$

where[30]

$$\sigma_B = \frac{[2+\frac{1}{2}y(1-\cos\theta)]^2 a_0^2}{4[1+\frac{1}{2}y(1-\cos\theta)]^4} \tag{12}$$

is the Born-approximation result, which is valid at large y, and

$$R(y) \equiv \frac{20}{4\pi y^{1/2}} \frac{(1+\frac{3}{2}y+0.8y^2+\frac{4}{20}\pi y^3)}{(1+0.103y^{-1/2}e^{-100y})(1+y^{5/2})}. \tag{13}$$

The total cross section obtained from Eq. (11) (by integrating over angles) agrees with the results for elastic electron scattering from hydrogen of Callaway *et al.*[31] at small y and those of Jhanwar, Khare, and Shobha[32] at intermediate y to within 20% for all y. This is comparable to the extent to which these theories agree with others.[32,33] The present cross section has the properties that at large y it yields the Born approximation while in the region $\sim 0.16 < ka_0 < \sim 0.5$ it reduces almost exactly to the Erginsoy result. At very small ka_0 the cross section does not, however, approach infinity as does that of Erginsoy. The use of the Born-approximation angular dependence in all regions is a simplification, but is qualitatively similar to the actual dependence.[32,33]

If the above cross section is used in connection with the second-order variational method (which is within ~0.2% of the infinite-order result) to calculate the mobility due to neutral impurity scattering alone of a single type of nondegenerate carrier, one obtains the result

$$\mu_N = \mu_E/H(z), \quad \mu_E = me^3/20\hbar^3\kappa_0 N_N, \quad z \equiv k_B T/E_B, \tag{14}$$

where μ_E is the Erginsoy result, m is the mass of the particle being scattered, and N_N and E_B are the density and binding energy of the impurities. The function $H(z)$ is plotted in Fig. 5. As might be expected, $H(z) \approx 1$ in the region $z \approx 0.1$, the main region for which Erginsoy's expression has been applied to neutral-impurity scattering.[34] The present mobility is, however, seen to be much larger than μ_E at high temperatures.

The exciton scattering case is similar except that

$$z \to (m/\mu_\pm)(k_B T/E_{ex}^\pm), \tag{15}$$

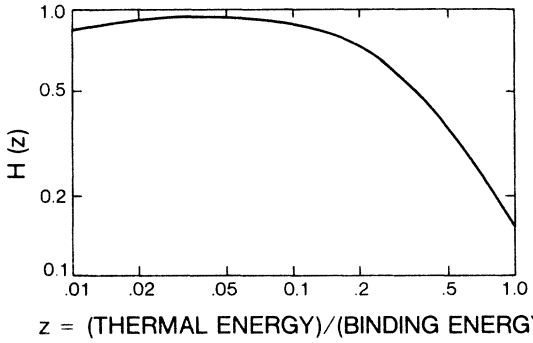

FIG. 5. $H(z)$ vs z, where H is the ratio of the neutral impurity mobility μ_E derived by Erginsoy to the present result μ_N, and z is the thermal energy $k_B T$ divided by the binding energy of the impurity E_B.

where m is the mass of the particle being scattered, and $\mu_\pm$ can be thought of as the reduced mass of the exciton, as calculated from the Bohr atom expression for the binding energy

$$E_{ex}^\pm = e^2/2\kappa_0 a_0^\pm = e^4\mu_\pm/2\kappa_0^2\hbar^2. \tag{16}$$

The cross section of Eq. (11) has been used to incorporate the scattering of both electrons and holes of arbitrary degeneracy by the two types of excitons into the first-order degenerate RPA result. (A convenient feature of the variational method is that the contributions due to the various scattering mechanisms can be calculated independently and then added in the various orders.) The results of this calculation for 21 K are shown as curve 4 of Fig. 2(g). It is seen that even at the lowest temperature studied, the decrease in conductivity due to exciton scattering is ~16% at the Mott-criterion density (discussed below). It should be noted, however, that the predicted unimportance of exciton scattering is a nontrivial result, since an indiscriminate application of the Erginsoy expression would have led to a conductivity decrease of nearly a factor of 2 at 10^{16} cm^{-3} and 21 K. Furthermore, it has been demonstrated that exciton scattering probably does significantly affect the transport properties of injected plasmas at temperatures below 21 K.

Quantitatively, the above should naturally not be taken too seriously because of the approximations used. In treating the excitons as neutral impurities, it has been assumed that they are of infinite mass, which is obviously not a good approximation. It should also be noted that whereas the static dielectric constant κ_0 has been incorporated into the hydrogen-atom model, no allowance has been made for screening by free carriers. Finally, above $z \approx 1$, inelastic scattering events will probably play a role.[35]

In dealing with the effects of the excitons, it must

be remembered that at some point a "Mott transition" is expected, that is, screening by mobile carriers should decrease the exciton binding energy to the point where the bound state disappears if the carrier density is too high. For a simple hydrogen-atom model this occurs when[13]

$$a_0 > 1.19\lambda, \tag{17}$$

where λ is the screening length. Using the Debye-Hückel result for λ (the system is nearly nondegenerate at the densities and temperatures of interest) and using $a_0 = 110$ Å [the smaller of the two Bohr radii, as derived from Eq. (16)] one obtains the criterion

$$n_M = 4.3 \times 10^{16}(T/100). \tag{18}$$

For the various temperatures, the transition densities predicted by Eq. (18) are given by the dashed lines of Fig. 2. A shift in the behavior of the experimental points in the region of the criterion is indeed readily apparent at all seven temperatures. [If one takes the hydrogen-atom model of the exciton more seriously than is probably justified, then above ~30 K one would actually expect two distinct transitions, the first occurring at densities slightly lower than the criterion of Eq. (18), corresponding to the two types of excitons. In fact, whatever change is occurring in the experimental behavior appears to begin at densities slightly less than those predicted by Eq. (18).]

The actual nature of the metal-insulator transition for excitons in germanium has not yet been determined in any conclusive way. Thomas and Rice have studied the near-infrared exciton luminescence for germanium at low temperatures (5.5 to 15 K) and report that the exciton line is still present at densities well above the expected Mott transition.[14] Instead of disappearing, the line broadens with increasing density, behavior which they attribute to the presence of trions (complexes containing two electrons and a hole or two holes and an electron). They argue that the exciton binding energy does not abruptly go to zero at the Mott criterion, but instead decreases very slowly.

The present data appear to support a gradual transition in that no sudden jumps in the conductivity are apparent. In fact, whereas the simple transition model predicts that the experimental points should abruptly join theoretical curves 2 at densities above the Mott criterion, the measured points are very slow to do so. Even if one suspects that the theory is inaccurate in the high-density region, there is no question that whatever manner of transition is occurring is quite gradual. A possible explanation is that the transition occurs at different injection levels in different parts of the sample because of nonuniformity. However, whereas the different samples varied with respect to uniformity of injected densities (sample 2, in particular, should always have been quite uniform), the conductivity results from the different samples are in excellent agreement at all densities. The behavior observed appears to be a general property of the material.

V. DISCUSSION

The validity of both the experiment and the theory will now be discussed in some detail. Beginning with the experiment, reasons for believing that the calibration of the carrier densities is essentially correct (except perhaps at the very highest densities at the lower temperatures) have already been given. It has also been noted that whereas the plasmas were not always strictly uniform, the effect on the measured conductivities was probably not large. Heating of the samples is seen to be ignorable if the amount of energy injected is compared with the specific heat of germanium as a function of temperature (although for temperatures very much below 21 K, heating would indeed be a problem at the higher injection levels). High-field effects were not a factor because the electric fields used in the measurements were never more than ~0.1 V/cm, and no field dependence of the conductivities was observed at those levels. Because strain caused by the different thermal expansion coefficients of the Ge and the contact materials can be shown by a crude calculation to fall off like the square of the ratio between the diameter of the contact and the distance away from it into the sample,[15] piezoresistance effects[36,37] should have been small. With regard to the extent to which the samples were doped during preparation, Hall measurements and low-temperature dark conductivity measurements indicated the values $|N_D - N_A| \approx 2 \times 10^{11}$ cm^{-3} for four of the five samples and ~10^{12} cm^{-3} for the fifth. Because the cross section for impurity scattering is comparable to that for electron-hole scattering, 10^{12} cm^{-3} impurities would have had little effect on the conductivity compared to 10^{14} cm^{-3} free carriers, the lowest injection level at which measurements were made (except for the case of the Xe flashlamp data at 72 K). Finally, it is noted that because the five samples had different thicknesses, surface quality,[15] and doping levels, most of the factors mentioned should have affected the different samples by different amounts. Yet apart from relatively minor fluctuations, the results obtained showed excellent agreement from sample to sample.

Most of the more obvious shortcomings of the previous theory of Appel have been dealt with in

the present treatment. While the use of the Born approximation was carried over from the previous theory, a comparison with the analysis of Blatt,[38] in which he examined the appropriateness of the Born approximation for nondegenerate electron-ion scattering, shows that the error introduced should have been small at the temperatures studied.[15] The incorporation of features such as screening of the phonon interactions,[39] the $\vec{q}$ dependence of the static dielectric constant,[40] and further generalization of the RPA screening approximation should also have relatively small effect at the temperatures and densities considered.

Although the theory would thus appear to be quite sound within the semiclassical framework (with the obvious exception of the apparent presence of an undetermined number of excitons at densities above the anticipated metal-insulator transition), there is reason for caution. First, the calculations have made no attempt to account for multiple-particle scattering processes except for the simple approximation of electron-exciton scattering. For example, whereas processes in which one electron is scattered by one hole have been considered, no attempt has been made to include events in which an electron is scattered by two or more holes simultaneously (or by an electron and a hole, etc.).

Although the authors know of no published work which deals with such processes in a way which permits direct comparison with the present problem, the qualitatively similar question of coherent multi-ion scattering in heavily doped semiconductors has received treatment. The calculation of Moore, in which he extended the Green's-function evaluations of the Kubo formula to include the lowest-order coherent scattering term,[41] was therefore roughly adapted to the present problem. The result was the prediction of a significant decrease of the conductivity for all temperatures at moderate and low densities. This is not necessarily surprising when it is considered that the screening distance is comparable to the interparticle spacing in this region.

The problem of converting the "adaptation" into a rigorous calculation is unfortunately more fundamental in nature than the matter of correcting the dynamics of the scattering processes. A qualitative difference between the two situations is that whereas the ions of the Moore calculation are randomly distributed, the carriers of the present case are capable of "correlating" themselves. Although it would be possible in principle to incorporate scattering processes involving more than two particles into the Boltzmann-equation description of transport theory, the more sensible approach would surely be a reformulation of the entire problem employing a many-body treatment.

On an even more fundamental level, moreover, the validity of the Boltzmann equation itself must be examined. A primary criterion is that the adiabatic principle be satisfied[42]

$$\hbar/k_B T < \tau , \tag{19}$$

where τ is the relaxation time of the carriers. Since the formulation assumes scattering between particles which are in specific momentum and energy states, the Boltzmann-equation approach is severely undermined by the uncertainty principle if the length of time that a typical carrier spends in a single state before it is scattered is too short for a well-defined energy to become established.

Using the approximation

$$\tau_i \approx \mu_i m_i / e , \tag{20}$$

where μ_i is the mobility of a particular type of carrier and m_i is its effective mass, the criterion reduces to

$$9.3(T/100)(\mu_i/10\,000)(m_i/0.125m_0) \gtrsim 1. \tag{21}$$

If the low-density mobilities given in the Appendix are assumed, the inequality is easily satisfied for electrons and heavy holes at all the temperatures studied. However, if one instead uses the actual mobility at the Mott criterion, the situation is somewhat marginal at the lower temperatures. A more detailed examination of these questions might help clarify the reason for the excellent agreement between experiment and theory at densities below the Mott criterion when such agreement is not necessarily anticipated.

VI. SUMMARY

For the first time, a systematic experimental study has sought to determine the electrical conductivity of a semiconductor, namely, germanium, as a function of uniform bipolar carrier density and temperature over a broad range of each parameter. The problem is one of fundamental importance in its own right as well as in connection with the study of high-density optically injected plasmas, an area of great current interest.

In addition, the most applicable previous theoretical treatment of the problem[10] has been improved in a number of respects, some of which significantly affect the calculated conductivity. At densities below the Mott criterion for exciton dissociation, excellent agreement between experiment and theory has been obtained. Although the anticipated metal-insulator transition is evident for each temperature at a density close to that predicted, the transition ap-

pears to be gradual. The data for the lower temperatures might suggest that excitons are present even an order of magnitude above the Mott criterion. Exciton scattering has also been studied by treating the excitons as if they were neutral impurities. Although the effect on the conductivity is predicted to be small at the temperatures studied, the results also indicate that exciton scattering is probably an important mechanism at temperatures below those of the present experiment.

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APPENDIX

Table I gives the temperature-dependent values of various relevant germanium parameters which have been used. μ_{e0} and μ_{h0} are the low-density electron and hole phonon mobilities. The values listed represent a composite of the experimental results of Refs. 20 and 43–46. The values of the hole-absorption cross section at 3.39 μm have been estimated from Ref. 16.

TABLE I. Germanium parameters for various temperatures.

T (K)	μ_{e0} (cm^2/V sec)	μ_{h0} (cm^2/V sec)	σ_C(3.39 μm) 10^{-16} (cm^2)
298	4 000	2 090	1.7
215	6 640	4 490	2.0
124	16 400	15 200	1.91
72	40 000	45 600	1.57
48	74 000	80 300	
32	137 000	127 000	
21	260 000	191 000	

The following effective masses have been used in the calculations[46]

$$\frac{m_1}{0.086m_0}\ \frac{m_3}{1.52m_0}\ \frac{m_h}{0.347m_0}\ \frac{m_l}{0.043m_0}\ ,$$

where m_0 is the free-electron mass, m_1 and m_3 are the transverse and longitudinal electron masses, and m_h and m_l are the heavy and light-hole masses. The static dielectric constant κ_0 was taken to be 15.36.[27]

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