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The Anisotropy of Conductivity of *n*-Type Germanium in Strong D.C. Fields

By

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With 6 Figures in the Text

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The electric conductivity of *n*-type germanium at large d.c. field intensities has been measured in three directions of symmetry of the cubic lattice. From these data the repopulation of valleys of the conduction band has been determined. Measurements were done with three materials of different purity. The variation of repopulation between these materials can be explained qualitatively by the influence of Coulomb scattering at ionized impurities. The data are compared with those of NATHAN and theoretical data of FRANZ and REIK et al. The relations of these data to those of the current component perpendicular to the field direction (SASAKI et al.) are also given.

1. Introduction

The electric conductivity of *n*-type germanium becomes field dependent and anisotropic in strong electric fields whereas in the low field region where OHM's law holds, the conductivity is isotropic. SHIBUYA¹ has calculated the angle between current and field from the anisotropy of the effective mass known from cyclotron resonance measurements. Later experiments by SASAKI et al.² gave much larger angles than those calculated. The discrepancy was explained by the assumption of electron transitions from "hot" to "cool" valleys of the conduction band resulting in an enhanced anisotropy of the conductivity. The experiments were repeated by KOENIG³, KOENIG, NATHAN, PAUL and SMITH⁴ and SCHMIDT-TIEDEMANN⁵ using an improved geometry.

NATHAN⁶ reported conductivity measurements in three directions of symmetry of the cubic germanium lattice where current and field inten-

¹ SHIBUYA, M.: Phys. Rev. **99**, 1189 (1955).

² SASAKI, W., M. SHIBUYA, and K. MIZUGUCHI: J. Phys. Soc. Japan **13**, 456 (1958). — SASAKI, W., M. SHIBUYA, K. MIZUGUCHI, and G. M. HATYAMA: J. Phys. Chem. Solids **8**, 250 (1959).

³ KOENIG, S. H.: Proc. Phys. Soc. (London) **73**, 959 (1959).

⁴ KOENIG, S. H., M. I. NATHAN, W. PAUL, and A. C. SMITH: Phys. Rev. **118**, 1217 (1960).

⁵ SCHMIDT-TIEDEMANN, K. J.: Festkörperprobleme, Bd. 1, S. 122. Braunschweig: Vieweg & Sohn 1962.

⁶ NATHAN, M. I.: Phys. Rev. **130**, 2201 (1963).

sity are parallel. From the different conductivities in $\langle 001 \rangle$ and $\langle 111 \rangle$ directions he was able to calculate the repopulation of the valleys in the $\langle 111 \rangle$ case. There is no repopulation if the field has the $\langle 001 \rangle$ direction, because all four valleys are equivalent then, whereas in the $\langle 111 \rangle$ direction the population of the "cool" valley is at a maximum. In the Nathan-type experiment the accuracy in determining the repopulation is much larger than in the Shibuya-type experiment, as the angle between current and field is zero when the repopulation is at a maximum due to crystal symmetry. Furthermore, if this angle is not zero, there are at least three valleys with unequal temperatures and consequently unequal populations. This means an additional assumption for the ratios of valley populations when evaluating the data of SHIBUYA and co-workers. The latter argument was pointed out by NATHAN.

In this paper measurements similar to those of NATHAN are reported, however with samples of different purities. First of all the theoretical relations between current density, field intensity and carrier concentration of the valleys are discussed.

2. Theory of the anisotropic conductivity

Using the transformation theory of HERRING and VOGT⁷, SHIBUYA¹ calculated the tensor of the electric conductivity in the case of acoustic phonon scattering. REIK and RISKEN⁸ generalized the calculation by considering optical and intervalley phonon scattering as well. PRICE⁹ and — using REIK and RISKEN'S results — SCHMIDT-TIEDEMANN¹⁰ have shown that the results of the calculation can be brought into a form which is independent of the particular scattering mechanism under the assumption of isotropic relaxation times.

Since all measurements have been made in the $[1\bar{1}0]$ plain which is determined by the $\langle 001 \rangle$ and $\langle 111 \rangle$ directions, the presentation of the results can be confined to this plain. Let \vec{e} be a unity vector in field direction with components $(2^{-\frac{1}{2}} \sin(\Theta + \varepsilon), 2^{-\frac{1}{2}} \sin(\Theta + \varepsilon), \cos(\Theta + \varepsilon))$ where $\Theta + \varepsilon$ is the angle between field and $\langle 001 \rangle$ direction and Θ is the angle between current and $\langle 001 \rangle$ direction. The unity vectors \vec{h}_ρ shall have the direction of the valley axes. Then for each valley an "effective" field intensity E_ρ shall be defined:

$$E_\rho = E \left[1 + \frac{K-1}{2K+1} \{(1-3(\vec{h}_\rho \cdot \vec{e})^2)\} \right]^{\frac{1}{2}} \quad (1)$$

⁷ HERRING, C., and E. VOGT: Phys. Rev. **101**, 944 (1956).

⁸ REIK, H. G., and H. RISKEN: Phys. Rev. **126**, 1737 (1962).

⁹ PRICE, P. J.: Cited by NATHAN⁶ and by KOENIG et al.¹².

¹⁰ SCHMIDT-TIEDEMANN, K. J.: Philips Research Repts. **18**, 338 (1963).

so that according to REIK¹¹ $(E_\rho/E)^2$ is proportional to the electron temperature of the valley under consideration. E is the magnitude of the field intensity applied to the sample. The quantity K is defined as the ratio of effective masses m_l/m_t , m_l being in the direction of the valley axes and m_t perpendicular. This ratio is 20 for *n*-type germanium. For anisotropic relaxation-times K is the inverse ratio of effective mobilities, μ_t/μ_l according to KOENIG et al.¹². Let us call σ the field dependent conductivity in $\langle 001 \rangle$ direction, σ_0 OHM's conductivity and the ratio

$$\sigma/\sigma_0 = S(E).$$

The carrier density n_ρ in a valley will depend on the field direction and magnitude. However, the total concentration of carriers

$$\sum_{\rho=1}^4 n_\rho = 4 \cdot n_0$$

will be independent of the field as long as the field is not too large. Then the current component parallel to the field is

$$j_l = \frac{1}{4} \cdot \sum_{\rho=1}^4 j_l^{(\rho)} \quad (2)$$

where

$$j_l^{(\rho)} = \sigma_0 \cdot E \cdot \frac{n_\rho}{n_0} \cdot S(E_\rho) \cdot (E_\rho/E)^2.$$

The current component perpendicular to the field is

$$j_t = \frac{1}{4} \cdot \sum_{\rho=1}^4 j_t^{(\rho)} \quad (3)$$

where

$$j_t^{(\rho)} = \sigma_0 \cdot E \cdot \frac{n_\rho}{n_0} \cdot S(E_\rho) \cdot \left(-\frac{1}{2} \frac{d(E_\rho/E)^2}{d(\Theta + \varepsilon)} \right).$$

Assuming $S(E)$ proportional to $E^{-\frac{1}{2}}$ and $n_\rho = n_0$, the anisotropy calculated by SHIBUYA is given by Eqs. (2) and (3).

The longitudinal and transverse components of the currents $j^{(\rho)}$ as calculated by Eqs. (2) and (3), and the components of the total current j are displayed in Fig. 1. In this case $S(E)$ was assumed equal to E_c/E , where E_c is a constant. This corresponds to a field-independent drift velocity which is a good approximation to the experimental data at large

¹¹ REIK, H. G.: Festkörperprobleme, Bd. 1, S. 89. Braunschweig: Vieweg & Sohn 1962. Equations (25) and (26) in the approximation of equation (47).

¹² KOENIG, S. H., R. D. BROWN, III, and W. SCHILLINGER: Phys. Rev. **128**, 1668 (1962), chap. C.

field intensities. In addition, no repopulation was assumed: $n_p = n_0$. It is obvious from Fig. 1 that the transverse component j_t is determined mainly by the carriers in the "cool" valley #1, and this is in agreement

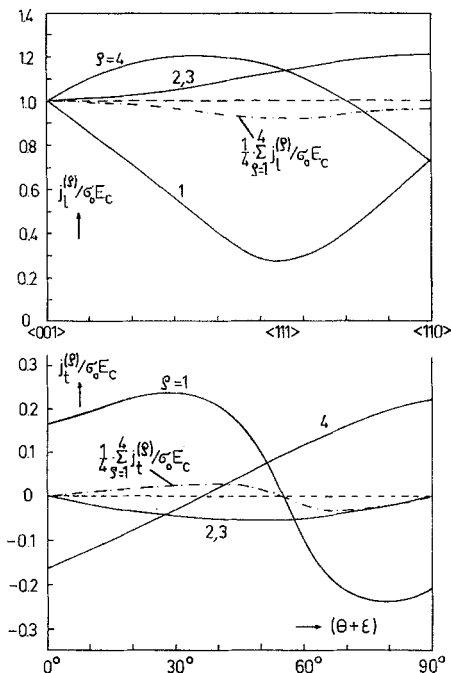


Fig. 1. Longitudinal and transverse components of current density due to the 4 valleys of the conduction band, as a function of the angle between the field and the $\langle 001 \rangle$ axes in the $[1\bar{1}0]$ plane of the crystal. It is assumed that all carriers were in the valley which is under consideration

with the interpretation given by SASAKI et al.². However, the longitudinal component j_l is determined mainly by the carriers in the "hot" valleys. This can be interpreted by use of Eqs. (2) and (1). Although these carriers are hot, their small effective mass makes their mobility higher than that of the cool, but at the same time heavy carriers in valley #1. This is due to the fact that the mobility is inversely proportional to the first power of the effective mass but only to the square root of the energy. The same argument applies to the total current, approximately, since the transverse component is small compared with the longitudinal component.

If the number of "immobile" cool carriers is increased by intervalley scattering at the expense of the mobile hot carriers, the current component j_l will be decreased and, according to Fig. 1, the anisotropy increased. For $\langle 111 \rangle$ and $\langle 110 \rangle$ directions of current the repopulation rate can easily be determined from the experimental data, because due to cubic symmetry of the crystal in the $\langle 111 \rangle$ case

$$\Delta n_2 = \Delta n_3 = \Delta n_4 = -\frac{1}{3} \Delta n_1,$$

where $\Delta n_p = n_p - n_0$, and in the $\langle 110 \rangle$ case

$$\Delta n_2 = \Delta n_3 = -\Delta n_4 = -\Delta n_1.$$

Now, instead of all n_p 's only Δn_1 need be considered. For simplification we call this Δn . Since Δn is the largest in a $\langle 111 \rangle$ field direction Eqs. (2) and (3) will be specialized for this case:

$$j_t = 0$$

$$j_l = \sigma \cdot E$$

with

$$\left. \begin{aligned} \frac{\sigma}{\sigma_0} &= \frac{1}{4} \cdot \left\{ \left(1 + \frac{\Delta n}{n_0} \right) \frac{\mu_1}{\mu_0} + 3 \left(1 - \frac{1}{3} \cdot \frac{\Delta n}{n_0} \right) \frac{\mu_2}{\mu_0} \right\} \\ \frac{\mu_1}{\mu_0} &= \frac{3}{1+2K} \cdot S \left(\sqrt{\frac{3}{1+2K}} \cdot E \right) \\ \frac{\mu_2}{\mu_0} &= \frac{1+8K}{3(1+2K)} \cdot S \left(\sqrt{\frac{1+8K}{3(1+2K)}} \cdot E \right). \end{aligned} \right\} \quad (4)$$

Experimental data will be reported for this, the $\langle 110 \rangle$ and the $\langle 001 \rangle$ directions of field, the latter being necessary for the determination of the function $S(E)$. From these data $\Delta n(E)$ will be calculated.

In short, let us discuss the other directions of field. Up to now, the n_ρ -values could be determined only approximately. PAIGE¹³ used $n_2 \approx n_3 \approx n_4$ where #1 again is the "cool" valley. A more accurate determination of the n_ρ 's has only been possible for warm electrons where $S(E) = 1 + \beta E^2$. Since both βE^2 and $\Delta n/n_0$ are small compared with 1, the product of both can be neglected:

$$\frac{n_\rho}{n_0} \cdot S(E_\rho) = \frac{n_\rho}{n_0} + \beta \cdot E_\rho^2. \quad (5)$$

Here β and, in a subsequent equation, γ are coefficients determined experimentally. SCHMIDT-TIEDEMANN¹⁰, considering the symmetry of the cubic lattice, was able to prove that

$$\frac{n_\rho}{n_0} = 1 + \left\{ \beta + \frac{\gamma}{2} \left(\frac{2K+1}{K-1} \right)^2 \right\} \cdot (E^2 - E_\rho^2). \quad (6)$$

For the region of very hot carriers with field-independent drift velocities REIK and RISKEN⁸ calculated the population ratios when the "cool" valley contains a maximum number of carriers:

$$\left(\frac{n_\rho}{n_0} \right)_{\max} = \frac{E/E_\rho}{\frac{1}{4} \cdot \sum_{\rho=1}^4 (E/E_\rho)}. \quad (7)$$

3. Experimental

The sample resistance was measured as a function of the applied d.c. field intensity using a Wheatstone bridge. The field was pulsed (0.1 μ sec, 30/sec) in order to avoid perceptible lattice heating. The bridge instrument was a 30 Mc/s-oscilloscope with difference preamplifier input. The shape of the sample is shown in Fig. 2. The sample was

¹³ PAIGE, E. G. S.: Proc. Phys. Soc. (London) **75**, 174 (1960).

etched with CP4. Both the free end of the filamentary part and the circumference of the disk were contacted using a Sn/Sb-solder. The negative pulse was applied to the free end of the filament. No injection was observed. In order to avoid sparking the cuts of the disk were filled with insulating foils. The sample resistance was corrected for the voltage drop across the circular base using an iteration method. The correction never exceeded 12% of the total resistance.

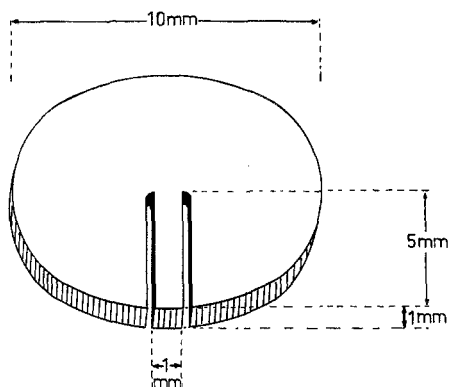


Fig. 2. Shape of samples. Field applied between the end of the filamentary part and the circumference of the disk

The etch pit density, the room temperature Hall mobility and the resistivities at room temperature and liquid nitrogen temperature were measured in order to obtain knowledge of the material used for the preparation of the samples. The data are compiled in Table 1 and proved quite normal.

In Fig. 3 the ratio of conductivities $\sigma(E)/\sigma_0$, which is equal to the corresponding ratio of mobilities $\mu(E)/\mu_0$ because of the field independent total carrier density, is plotted vs the field intensity E for the 5 ohm-cm samples. Both conductivities $\sigma(E)$ and σ_0 are somewhat different from sample to sample because of fluctuations in doping, and this is eliminated by taking the ratio. It is obvious from Fig. 3 that the difference between the $\langle 001 \rangle$ and the $\langle 111 \rangle$ data is largest at 85 °K and several kV/cm.

Table 1. Etch pit density EPD on $\langle 111 \rangle$ face, room temperature mobility $\mu_0 = 8 \cdot \mu_{\text{Hall}} / 3\pi$ at low field intensities, resistivities ρ_0 at 295.5 and 79°K and carrier densities n of the samples with three different orientations.

The carrier densities are equal to the corresponding ionized impurity densities if no compensation is assumed.

Sample	Orientation	EPD cm ⁻²	μ_0 cm ² /Vsec	ρ_0 (295.5°K) Ohm-cm	ρ_0 (79°K) Ohm-cm	n cm ⁻³
10 Ω-cm	$\langle 001 \rangle$	3000	3200	11.5	1.31	$1.69 \cdot 10^{14}$
	$\langle 110 \rangle$		3200			
	$\langle 111 \rangle$		3100			
5 Ω-cm	$\langle 001 \rangle$	3700	2700	5.0	0.63	$4.63 \cdot 10^{14}$
	$\langle 110 \rangle$		2400			
	$\langle 111 \rangle$		2400			
2 Ω-cm	$\langle 001 \rangle$	1300	3100	1.99	0.296	$1.01 \cdot 10^{15}$
	$\langle 110 \rangle$		2800			
	$\langle 111 \rangle$		3100			

Anisotropy is found at 273 °K although very much smaller than at low temperatures. For the 2 ohm-cm and the 10 ohm-cm samples the curves are similar to those shown except that at 273 °K no anisotropy is detectable.

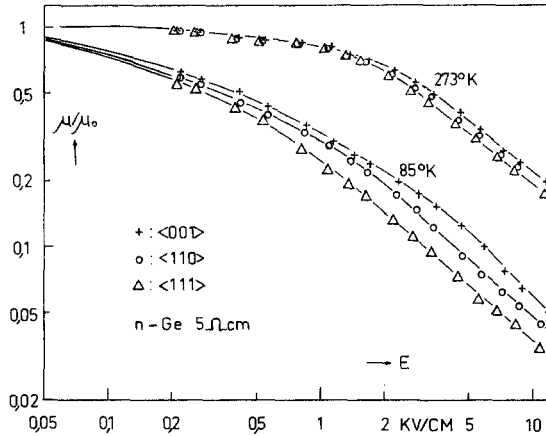


Fig. 3. Mobility ratio for three orientations vs field intensity. Lattice temperatures 85 and 273 °K. The experimental error is approximately given by the vertical dimension of the signs

Table 2
Values of α for $\langle 001 \rangle$ samples

Sample	$\alpha_{85^\circ K}$	$\alpha_{273^\circ K}$
10 Ω -cm	0.87	0.84
5 Ω -cm	0.975	0.78
2 Ω -cm	0.70	0.93

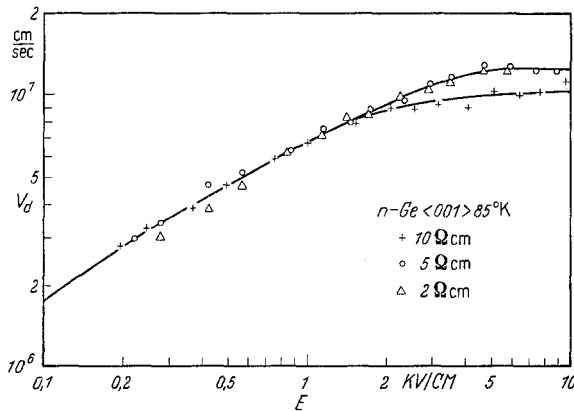


Fig. 4. Drift velocity vs field intensity for $\langle 001 \rangle$ orientation of three samples of different purity

At field intensities of more than 2 kV/cm all curves can be approximated by a power law

$$\sigma/\sigma_0 \propto E^{-\alpha}$$

where α is a constant. The values of α are tabulated in Table 2 for the $\langle 001 \rangle$ curves. The value $\alpha=1$, corresponding to a constant drift velocity, is never reached. For field directions different from $\langle 001 \rangle$ the shapes of the curves are influenced by intervalley transitions.

In Fig. 4 the drift velocity v_d vs field intensity is plotted for the $\langle 001 \rangle$ samples. v_d is obtained from the data shown in Fig. 3, and the values of μ_0 as given by Table 1. For all dopings the data are represented by the same curve except at fields of more than 2 kV/cm where the 10 ohm-cm data are somewhat below the others. No explanation is available for this exception.

4. Discussion

Fig. 5 displays the experimental data of μ/μ_0 vs E already shown in Fig. 3. Now values of μ/μ_0 calculated for the $\langle 111 \rangle$ field direction with no repopulation are given by a dashed curve. Comparison of this

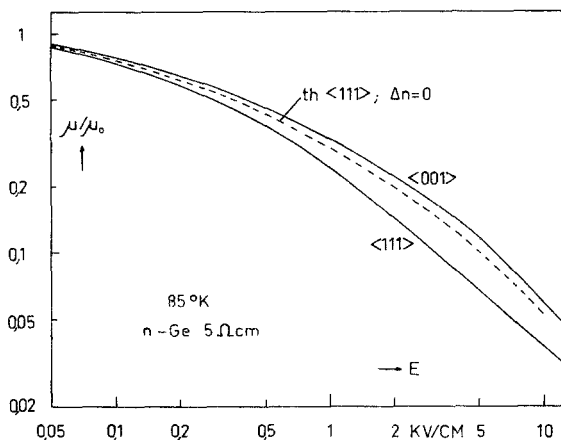


Fig. 5. Comparison of $\langle 111 \rangle$ mobility ratios. Lower curve: Experimental. Dashed curve: Theoretical for no repopulation of valleys. Upper curve: $\langle 001 \rangle$ mobility ratio (no repopulation)

with the experimental $\langle 111 \rangle$ curve shows the factor by which the anisotropy is increased due to a repopulation of the valleys, in agreement with the theory presented in this paper. In comparing the $\langle 001 \rangle$ and $\langle 111 \rangle$ experimental data of σ/σ_0 and using Eqs. (4) the relative increase in population of the "cool" valley $\Delta n/n_0$ was calculated and plotted vs E in Fig. 6. NATHAN's data obtained with 18 ohm-cm material at 77 °K are given by a dash-dotted curve for comparison. The dashed

curve represents theoretical data calculated by FRANZ¹⁴ for a pure sample. The dashed line indicates the limiting value calculated by REIK and RISKEN using Eqs. (7).

Considering the room temperature resistivities NATHAN's sample was purer than the ones used in this paper. Its data should therefore be nearest to the theoretical curve. The agreement is tolerable if the convergence problems of the Franz calculation are taken into account. The experimental curves have their maxima at larger field intensities for less sample purity, and at the same time the maximum values are

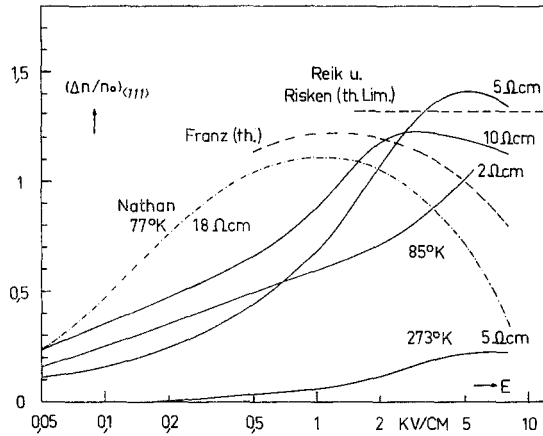


Fig. 6. Relative increase in population of the "cool" valley for samples of different room temperature resistivity, the direction of field being that of the rotational axes of the valley $\langle 111 \rangle$. Dashed curves: Theoretical. Dash-dotted curve: Experimental by NATHAN

larger. The shift seems to be proportional to the density of ionized impurities. It can be explained qualitatively in the following way: Carriers scattered at ionized impurities do not get quite as hot as in a pure material. Because of the lower carrier energy the repopulation of valleys will be less accordingly. In addition, the intervalley transition probability is influenced by Coulomb scattering as observed by WEINREICH et al.¹⁵. When comparing Figs. 4 and 6 it is apparent that the repopulation is influenced by Coulomb scattering much more than the $\langle 001 \rangle$ drift velocity. The repopulation ratio was also calculated for the case of a field in $\langle 110 \rangle$ direction. At 85 °K and field intensities of less than 2 kV/cm it is less than 20% and within the experimental error agrees well with calculations by FRANZ and by REIK and RISKEN. Above

¹⁴ FRANZ, W.: Phys. stat. sol. 3, 1260 (1963).

¹⁵ WEINREICH, G., T. M. SANDERS jr., and H. G. WHITE: Phys. Rev. 114, 33 (1959); a theory has been presented by P. J. PRICE and R. L. HARTMAN, J. Phys. Chem. Solids 25, 567 (1964).

2 kV/cm the 5 and 10 ohm-cm curves show a steep increase up to 80% which cannot be understood.

Finally, let us discuss the nonparabolicity of the $\langle 111 \rangle$ valleys at elevated energy values and the influence of scattering between nonequivalent valleys on the mobility of hot carriers. Since the [000] valley in germanium is below the $\langle 100 \rangle$ valleys the value of m_i will increase with increasing energy more than the m_t values, and the result is an increase of K with energy. Since the equations of this paper are very insensitive with respect to an increase of K above 20, the effect of the nonparabolicity of the $\langle 111 \rangle$ valleys on the anisotropy can be neglected. The effect of nonequivalent intervalley scattering was pointed out by RISKEN and MEYER¹⁶ and discussed in more detail by PAIGE¹⁷. According to PAIGE the number of carriers in the $\langle 100 \rangle$ valleys relative to those in the $\langle 111 \rangle$ valleys is $6 \cdot \exp(0.21 \text{ eV}/kT_e)$ where T_e is the carrier "temperature" and 0.21 eV is the energy difference of the valleys. The [000] valley was neglected. Consequently at a lattice temperature of 80 °K and field intensities of several kV/cm 6/7 of the carriers should populate the "silicon-like" $\langle 100 \rangle$ valleys. The mobilities in these valleys may be assumed equal to those found with n -type silicon. As a consequence, the anisotropy of the conductivity of n -type germanium at high field intensities should be reversed and similar to that observed with n -type silicon¹⁸ which is obviously not the case. Considering the large uncertainty of ± 0.3 eV in the energy difference of the valleys as quoted by PAIGE we feel the upper limit to be more realistic and the effect of these valleys on the hot carriers to be less important for the range of field intensities under discussion.

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¹⁶ RISKEN, H., and H. J. G. MEYER: Phys. Rev. **123**, 416 (1961).

¹⁷ PAIGE, E. G. S.: Progr. in Semicond., Vol. 8. London 1964.

¹⁸ J. RGENSEN, M. H., N. I. MEYER, and K. J. SCHMIDT-TIEDEMANN: Int. Conference on the Physics of Semicond. Paris 1964, p. 457.