

we can raise the calculated gap to agree with experiment if we raise the energy of the main peak also. For Mg_2Ge and Mg_2Sn we notice that the gaps are both bigger than the experimental values, but since the spin-orbit interaction lowers these gaps, the agreement with experiment will be better if spin-orbit effects are included. The calculations show that the fundamental gaps are indirect; for Mg_2Si and Mg_2Ge , this appeared to be consistent with experiment.²³

E. Comparison with Existing Calculations

If we compare our results with the two existing calculations for Mg_2Si , we find that our results are radically different from Folland's¹⁴; however, we find that Lee's¹³ results are similar to ours with some shifts in the energies. The energy differences can be traced in part to the magnesium potential which was used in the two calculations. If we look at Fig. 7 and Table I, we see that there is considerable contribution from the magnesium potential for $|k| > 2k_F$. However, in Lee's calculations

²³ P. H. Koenig, D. W. Lynch, and G. C. Danielson, *J. Phys. Chem. Solids* **20**, 122 (1961).

an exponential tail function which vanishes at about $|k| = 2.4$ a.u. for $|k| > 2k_F$ was used. Thus Lee's effective pseudopotential [i.e., $V(|G|)$ in Table I] is bigger on the average, resulting in bigger energy differences. We would, therefore, expect an $\epsilon_2(\omega)$ curve derived from Lee's band to be similar to ours in shape, but the main structure would have higher energies compared with our result. Inspection shows that the shift in energy is about 1 eV.

In conclusion, we would say that our calculations quite successfully explain the data on Mg_2Si , Mg_2Ge , and Mg_2Sn . The band structures were calculated to fit optical structure using potentials which are consistent with those used in existing calculations for other crystals. We note that the minor structure in the measured optical spectra are also reproduced in the calculations.

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Longitudinal Anisotropy of the High-Field Conductivity of *n*-Type Germanium at Room Temperature

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New pulse measurements of the high-field conductivity of *n*-type germanium at room temperature have been performed. Contrary to previous measurements, the conductivity is anisotropic above the Ohmic field range. The highest current for a given field is found along the $\langle 100 \rangle$ crystallographic axes; the $\langle 110 \rangle$ current is as much as 9% lower, and the $\langle 111 \rangle$ current 14% lower than the $\langle 100 \rangle$ current. The maximum anisotropy is found at a field of 3 kV/cm. No region of constant drift velocity is found; current increases with field up to 30 kV/cm, the highest field applied.

1. INTRODUCTION

IN contrast to the situation in the low-field, Ohmic region, the magnitude of the current for a given high field is expected to, and has in general been found to depend on current direction in *n*-type Ge. Several measurements of the longitudinal anisotropy of the high-field conductivity of *n*-type Ge have been reported.¹⁻⁴ This anisotropy is a result of the many-valley conduction-band structure of Ge, and the effective-mass anisotropy of the individual valleys. The rate at which electrons absorb energy from the electric field depends on the relative orientations of the valley and field, being highest when the field is along an "easy," or low-

mass direction of the particular valley. The high-field mobility is a decreasing function of electron temperature, so the rate at which the contribution of electrons in a particular valley to the total current deviates from Ohmic behavior depends on the orientation of that valley relative to the field. In the low-field region, the anisotropic parts of the single-valley conductivities cancel, and the total conductivity is a scalar. Since the single-valley mobilities have different field dependences, this cancellation does not continue into the high-field region, and the high-field conductivity is not, in general, isotropic.

The above discussion has implicitly assumed that the electrons are evenly distributed among the four equivalent $\langle 111 \rangle$ valleys of the conduction band, which is not necessarily true. This distribution can be shifted by equivalent intervalley scattering. In relatively pure Ge,

¹ R. Barrie and R. R. Burgess, *Can. J. Phys.* **40**, 1056 (1962).

² M. I. Nathan, *Phys. Rev.* **130**, 2201 (1963).

³ V. Dienys and J. Pozhela, *Phys. Status Solidi* **17**, 769 (1966).

⁴ M. Dienene, V. Dienys, and J. Pozhela, *Lietuvos Fiz. Rinkiny* **6**, 431 (1966).

equivalent intervalley scattering of electrons can occur by means of emission or absorption of a $\langle 100 \rangle$ phonon from near the zone edge with energy of about 300°K. At lower lattice and electron temperatures, the most prominent process is scattering of an electron from a hotter to a cooler valley with the emission of a phonon, resulting in a slow transfer of electrons to the cooler valleys from the hotter ones. This repopulation enhances the anisotropy described above. Because of the low scattering rate in this situation, intervalley scattering has a negligible influence on energy relaxation. At higher lattice or electron temperatures, intervalley scattering becomes an important energy relaxation process, and tends to equalize the electron temperatures in all of the valleys.³ Then the valleys tend towards equal populations and conductivities, and the total conductivity becomes isotropic. So the effects of intervalley scattering on the high-field conductivity are (1) At some low-field strength just above the Ohmic range the longitudinal anisotropy has a maximum; (2) at higher-field strengths the anisotropy tends to vanish; and (3) the anisotropy is smaller at higher-lattice temperatures. These effects are reflected in the previously reported experiments.

Previous measurements are in general agreement that the currents for a given field are related by

$$I_{\langle 100 \rangle}(E) \geq I_{\langle 110 \rangle}(E) \geq I_{\langle 111 \rangle}(E), \quad (1)$$

where the subscripts refer to the current direction. The $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions have usually been chosen for measurements because symmetry was thought to require that current and field be parallel in these directions. At 77°K the experimental results consistently show a maximum in the anisotropy at 1–2 kV/cm, satisfying the inequalities of Eq. (1). At fields of several times 10⁴ V/cm, Barrie and Burgess found the anisotropy to vanish; other measurements have not been carried to such high-field strengths, but all tend toward isotropy at the highest fields reported.

At room temperature the previously reported experimental results are not in agreement. Early measurements by Nathan, and by Barrie and Burgess, using pulse techniques, found the room-temperature conductivities in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions to be the same, within their experimental uncertainties, for fields strengths to 10 (Nathan) and 75 kV/cm (Barrie and Burgess). However, Dienys and Pozhela, using the microwave technique described earlier by Zucker, Fowler, and Conwell,⁵ found the $\langle 111 \rangle$ conductivity to be as much as 14% below that in the $\langle 100 \rangle$ directions at room temperature; they reported no results for the $\langle 110 \rangle$ directions at either 77°K or 300°K.

Measurement of conductivity in the $\langle 110 \rangle$ directions

³ J. Zucker, V. J. Fowler, and E. M. Conwell, *J. Appl. Phys.* **32**, 2606 (1961).

is complicated by the possibility of a Sasaki effect⁶ (current and field not parallel) in this direction. Calculations by Reik and Risken⁷ suggest that for current directions near $\langle 110 \rangle$ in the Sasaki plane (the plane containing a $\langle 110 \rangle$ and the $\langle 001 \rangle$ normal to it), electric field direction is a triple-valued function of the current direction. For current exactly in the $[110]$ direction there are, in addition to the situation with current and field parallel as required by symmetry, situations with equal, but oppositely directed components of field along the $[001]$ direction.

Erlbach⁸ has considered the possibility of a transverse negative mobility in *n* Ge. In unstrained Ge, Erlbach suggested that the $\langle 110 \rangle$ directions would most nearly satisfy the criteria for the existence of the effect. But at 300°K, the amount of intervalley transfer reported by Nathan² is too small for the appearance of the transverse negative mobility. If the effect were present, though, it might manifest itself in the instability of the situation with current and field parallel, described in the last paragraph.

Recently, Shyam and Kroemer⁹ have reported observation at room temperature of polarization along a $[001]$ direction, the configuration described above. They claim that this polarization is switched in sign by application of a small transverse electric field before application of the high-current pulse. They interpret this as switching between the two nonparallel field directions suggested by Reik and Risken. The parallel state is not stable because of the Erlbach effect. Kroemer has suggested that this experimental observation indicates a larger amount of intervalley transfer at room temperature than reported by Nathan, and that the result is not consistent with the absence of longitudinal anisotropy at 300°K.

Dienys and Pozhela do not directly measure the $\langle 110 \rangle$ current-voltage characteristic. They do measure the low-field time-average conductivity for current in the $[001]$ direction as a function of the peak magnitude of a strong microwave-frequency electric field along the $[110]$ direction: They relate this quantity to the $\langle 110 \rangle$ high-field conductivity. They do not give values for this quantity above 1500 V/cm, possibly because of the onset of the Erlbach effect.

Because of the apparent contradiction between pulse and microwave measurements of longitudinal anisotropy at room temperature, and the inconsistency of the results of Shyam and Kroemer with the earlier pulse measurements, we have performed a new set of pulse measurements at room temperature, with somewhat greater precision than the earlier measurements.

⁶ W. Sasaki and M. Shibuya, *J. Phys. Soc. Japan* **11**, 1202 (1956); W. Sasaki, M. Shibuya, and K. Mizuguchi, *ibid.* **13**, 456 (1958); W. Sasaki, M. Shibuya, K. Mizuguchi, and G. M. Hato-yama, *J. Phys. Chem. Solids* **8**, 250 (1959).

⁷ H. G. Reik and H. Risken, *Phys. Rev.* **126**, 1237 (1962).

⁸ E. Erlbach, *Phys. Rev.* **132**, 1976 (1963).

⁹ M. Shyam and H. Kroemer, *Appl. Phys. Letters* **12**, 283 (1968).

2. EXPERIMENTAL DETAILS

Samples were prepared from As-doped Ge, having room-temperature resistivity of $3.5 \Omega \text{ cm}$ and carrier concentration of $4.5 \times 10^{14} \text{ cm}^{-3}$. $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ wafers of the material were cut from adjacent portions of the same crystal, lapped, and polished to a thickness of 0.089 cm; all three were simultaneously lapped and polished to minimize differences between the lengths of the samples. $n+$ contact regions were formed on the faces of the wafers by shallow diffusion of As into the Ge. Once again, all three wafers were handled at the same time to ensure that the samples would be, apart from orientation, as nearly identical as possible. After diffusion, the wafers were plated with a thin layer of nickel followed by gold. They were then cut into individual samples with a square cross section 0.071 cm on a side. Gold leads, 0.008 cm in diameter, were attached to the ends of the samples with low-melting-point indium-alloy solder. The contacts and leads were masked with a mixture of "black wax" and trichloroethylene, and the samples etched in CP4 at room temperature. (Measurements on samples which had not been etched showed evidence of a large surface current, previously described by Nag and Paria,¹⁰ which hampered the determination of the anisotropy of the bulk conductivity. The etching reduced the magnitude of this current to below that which we could detect.)

The current-voltage characteristics of the samples were determined by using 5-nsec pulses and a two-channel sampling oscilloscope. The current pulses were flat-topped (except for an initial transient), indicating the absence of carrier injection at the contacts. The resulting current-voltage characteristics were independent of polarity for all samples from which data were used. The results were normalized to the same low-field conductance for all samples, to allow for slight differences in cross-sectional areas; the unadjusted low-field conductances were generally within 2% of each other, indicating a lack of any serious irregularities. The majority of the normalized curves for a given orientation were within 5% of each other throughout the field range covered by these measurements. However, several samples lay well outside this range, and these samples were rejected on purely statistical grounds. The data presented in this paper are the averages of the results for four or five samples of each orientation. Among the "good" samples of a particular orientation, scatter in the data is greatest around 3 kV/cm, the region of greatest curvature in the current-voltage characteristic, and of greatest anisotropy.

3. RESULTS AND DISCUSSION

The data are presented in the form of velocity-field curves in Fig. 1. The field is the longitudinal field, the potential drop along the sample divided by sample

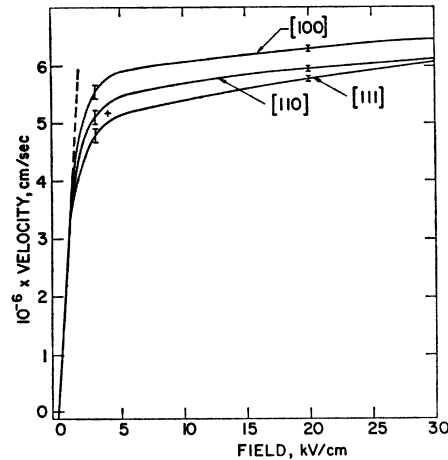


Fig. 1. Drift velocity versus electric field strength at room temperature. The dashed line is an extension of the low-field linear region, where the mobility is assumed to be $3800 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. Solid lines are experimental results for the current directions indicated on the figure. Typical uncertainties are shown by the error bars at 4 and 20 kV/cm. +, $\langle 110 \rangle$ current calculated from Kroemer's $\langle 100 \rangle$ - $\langle 110 \rangle$ anisotropy calculation, normalized to the experimental $\langle 100 \rangle$ current at 4 kV/cm.

length; no attempt has been made to correct the $\langle 110 \rangle$ data for the Sasaki effect. Space-charge effects should be negligible in samples of the length and carrier concentration chosen for this work. The drift velocity is determined by assuming that the low-field drift mobility is $3800 \text{ cm}^2/\text{V sec}$.

As shown in Fig. 1, we find a maximum in the room-temperature anisotropy at a longitudinal field strength of about 3 kV/cm. Here the $\langle 110 \rangle$ velocity is about 9% below, and the $\langle 111 \rangle$ about 14% below the velocity for current in a $\langle 100 \rangle$ direction. The $\langle 100 \rangle$ - $\langle 111 \rangle$ anisotropy is in good agreement with the microwave results of Dienys and Pozhela for the range of electric field strength covered by both experiments. While the anisotropy persists in the highest fields applied, it does decrease as suggested by the simple model given above. The magnitude of the anisotropy is very much smaller than is found at liquid-nitrogen temperature.

Kroemer¹¹ has calculated the $\langle 100 \rangle$ - $\langle 110 \rangle$ longitudinal anisotropy at a longitudinal field strength of 4 kV/cm, and our results are in good agreement with this calculation. Unfortunately, his technique is not applicable to the $\langle 100 \rangle$ - $\langle 111 \rangle$ anisotropy, nor to a very wide range of fields. A quantitative theoretical treatment of the longitudinal anisotropy was not available at the time of this work, so we are unable to make a detailed comparison of these results with theory.

The drift velocities shown in Fig. 1 are in good agreement with previously reported values.¹² But we see no region of saturated drift velocity as has been previously

¹¹ H. Kroemer (private communication).

¹² See E. M. Conwell, in *High-Field Transport in Semiconductors*, Suppl. 9 to *Solid State Phys.*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1966) for a review and references covering the region of constant drift velocity in Ge.

¹⁰ B. R. Nag and H. Paris, *Brit. J. Appl. Phys.* 17, 71 (1966).

reported.^{1,2,12,18} A number of calculations have indicated the existence of such a region, but they all fail to include the effects of intervalley scattering to the $\langle 100 \rangle$ valleys. We have previously reported the existence of a bulk negative differential conductivity (BNDC) in strained *n* Ge which is due to intervalley transfer between the strain-split $\langle 111 \rangle$ valleys of the conduction band.¹⁴ The threshold field for the onset of oscillations due to this effect occurs when a significant number of electrons have been excited by the field to states in which transfer from the low-energy high-mobility valley to the higher-energy lower-mobility valley is possible. For strain-induced valley splittings of the order of the 0.18 eV, separation of the $\langle 111 \rangle$ and $\langle 100 \rangle$ valleys in unstrained Ge,¹⁶ this threshold is well below the range of fields in which saturated drift velocity has been reported. Thus, the theoretical approximations which account for saturation in this region are never valid because of the influence of scattering processes involving the $\langle 100 \rangle$ valleys. A number of authors¹⁶ have recently discussed the necessity of inclusion of non-equivalent intervalley scattering in any proper treatment of the hot electron problem in *n*-type Ge, and have reached this same conclusion for differing reasons.

At 77°K, previous experiments have shown exact saturation only in the $\langle 100 \rangle$ directions. The quantities actually measured in these experiments (as in the present work) are sample current versus voltage drop along the sample. Shockley¹⁷ has shown that only in the case where there is no BNDC can velocity-field curves be simply deduced from such data. If there is a region of BNDC, exact saturation will be observed in the corresponding region of the current-voltage characteristic. Elliott, Gunn, and McGroddy¹⁸ have reported the existence of BNDC in unstrained Ge at 77°K for the situation where the current and field are along a $\langle 100 \rangle$ direction; the range of field strength over which the BNDC is observed is in fair agreement with the range of saturation previously reported. It seems likely

that these earlier experiments, performed with circuitry, sample size, geometry, and carrier concentrations unfavorable for the observation of the oscillations associated with the BNDC, should be interpreted as a reflection of the BNDC rather than saturation of the velocity-field curve.

The explanation given above of the saturation of the 77°K current-voltage characteristics is not applicable to the room-temperature results. The BNDC in unstrained Ge has not been observed above 150°K. When experimental uncertainties are taken into account, a small positive slope in the saturation region of the current-voltage curves is consistent with earlier measurements. The data shown in Fig. 1 have a higher slope than is consistent with the uncertainties in the earlier measurements, but the extreme limits of the uncertainties do overlap. Saturation is not consistent with the present measurements. Interpretation of past experiments might have been somewhat prejudiced by the observed saturation at 77°K and its theoretical justification.

4. CONCLUSION

In conclusion, we have performed new measurements of the high-field conductivity of *n*-type Ge at room temperature using pulse techniques. We find anisotropy at all fields above the Ohmic range to 30 kV/cm, the highest fields applied. The results are in agreement with the $\langle 100 \rangle$ - $\langle 111 \rangle$ anisotropy deduced from microwave measurements. The $\langle 100 \rangle$ - $\langle 110 \rangle$ anisotropy at 4 kV/cm is in agreement with a recent calculation, which is, unfortunately, limited in validity to these orientations and to field strengths near 4 kV/cm. Contrary to previous experimental results, no saturation of the current-voltage characteristic is observed, and we conclude that there is no saturation of the velocity-field curve. This is also evidence for the absence of BNDC at room temperature in unstrained Ge of any of the three orientations considered in this work.

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¹³ J. B. Gunn, *J. Electron* **2**, 87 (1956).

¹⁴ J. E. Smith, Jr., *Appl. Phys. Letters* **12**, 233 (1968).

¹⁵ A. Jayaraman, B. B. Kosicki, and J. C. Irvin, *Phys. Rev.* **171**, 837 (1968).

¹⁶ H. Risken and H. J. G. Meyer, *Phys. Rev.* **123**, 416 (1961); E. M. Conwell, *ibid.* **135**, A1138 (1964); E. G. S. Paige, *Progr. Semicond.* **8** (1964); N. I. Meyer and M. H. Jørgensen, *J. Phys. Chem. Solids* **26**, 823 (1965); M. H. Jørgensen, thesis, The Technical University of Denmark, 1966 (unpublished).

¹⁷ W. Shockley, *Bell System Tech. J.* **33**, 799 (1954).

¹⁸ B. J. Elliott, J. B. Gunn, and J. C. McGroddy, *Appl. Phys. Letters* **11**, 253 (1967).