

## Temperature Dependence of the Piezoresistance of High-Purity Silicon and Germanium

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The change of resistance in uniaxial compression has been measured for a number of single-crystal specimens of high-resistivity *n*- and *p*-type germanium and silicon over the ranges 5° to 350°K (Ge) and 20° to 350°K (Si). For *n*-type material in the orientations giving the large effect—[110] for *n*-Ge and [100] for *n*-Si—the piezoresistance is, as predicted by theory, linear in  $T^{-1}$  over most of the temperature range and with a small intercept. It is rather insensitive to impurity scattering. The departure from linearity in  $T^{-1}$  due to the onset of intervalley scattering near room temperature is estimated theoretically; it appears to be just barely detectable for *n*-Ge. The small piezoresistance of [100]-oriented *n*-Ge varies little with temperature over most of the extrinsic range, again in accordance with theory. For *p*-Ge the results suggest that ideally pure material would show a piezoresistance dominated by a  $T^{-1}$  term for both [110] and [100] orientations. It is shown that this is to be expected theoretically,

although the mechanism of piezoresistance for a degenerate band is more complicated than for a many-valley model. However, the results for *p*-type material are, as they should be, much more sensitive to impurity scattering, even the sign of the effect varying with the purity for [100] specimens. For *p*-Si no simple temperature dependence is found, presumably because the spin-orbit splitting of the bands is comparable with  $kT$ . At temperatures low enough to condense most of the carriers onto impurity centers, the piezoresistance departs from linearity in  $T^{-1}$  and varies from specimen to specimen. This behavior appears not to be due to impurity scattering; it may be caused in part by inhomogeneities. Surface conduction effects have been observed, but can be eliminated by etching. Neither Hall nor piezoresistance measurements reveal any detectable variation of the ionization energy of donors with strain. No departure of the piezoresistance from linearity in the applied stress has been observed.

### 1. INTRODUCTION

THE discovery by Smith<sup>1</sup> of the large effect of elastic strain on the resistivity of some semiconductors opened up interesting possibilities for learning useful things about the conduction process. As was pointed out by Smith, the anisotropy of this “piezoresistance” effect can indicate the orientations of the band-edge points of a “many-valley” semiconductor. Also, the effect is directly proportional to the value of a deformation-potential constant which occurs in the theory of mobility.<sup>2-4</sup> For this reason, and because a careful study of piezoresistance seemed likely either to strengthen our present picture of conduction in silicon and germanium or else to uncover important defects in it, the present study was undertaken. It differs from the work of Smith primarily in covering as wide a temperature range as can conveniently be studied for high-resistivity extrinsic material, namely, from 5° to 350°K for *n* and *p* germanium, and from 20° to 350°K for *n* and *p* silicon.

The piezoresistance phenomenon relates the change  $\delta\rho$  of the resistivity tensor to the stress  $\chi$  or the strain  $u$ . If we designate components of all symmetric tensors with an index  $r$  which runs from 1 to 6, as is customary in the theory of elasticity, we can define a piezoresistance tensor  $\Pi$  or an elastoresistance tensor  $\mathbf{m}$  by

$$\delta\rho_r/\rho_0 = \sum_s \Pi_{rs} \chi_s = \sum_s m_{rs} u_s. \quad (1)$$

For a cubic substance  $\Pi$  or  $\mathbf{m}$  can be described in terms of its 11, 12, and 44 components referred to coordinate axes chosen along the cube directions. For silicon and germanium some of these components are very much

larger than the others. As we shall discuss later on, theory<sup>2-4</sup> makes fairly detailed predictions about the behavior of these large components, and it is to them that we have devoted the greatest attention. One of the principal predictions is that the large components should be nearly proportional to  $1/T$  over a wide range of temperature. This has recently been confirmed by Keyes.<sup>5</sup> Fortunately, these large components—unlike some of the others—can be measured by measuring the resistance of a rod in simple longitudinal tension or compression, and we have used this method in nearly all of our work. Details are given in the next section. After presentation of the raw results, we shall discuss the relation of theory to the many interesting features of the data.

### 2. EXPERIMENT

Our measurements covered the isothermal piezoresistance, electrical conductivity, and Hall coefficient of silicon and germanium as functions of temperature. Temperatures over the desired range—5° to 350°K for germanium and 20° to 350°K for silicon—were achieved with a three-wall cryostat having a nitrogen-cooled radiation shield. For thermal control, a brass can containing charcoal and wound with a heater was located at the bottom of the inner Dewar. The sample was mounted on the holder shown in Fig. 1 as it would appear with the cryostat removed. The thermal capacity of the holder and of the refrigerant adsorbed on the charcoal gave sufficient thermal stability to allow a complete set of measurements to be made at any intermediate temperature. For example, the temperature drift at 10°K without pumping was about 0.2° per hour. Temperature below 20°K was measured with a carbon resistance thermometer calibrated against a

<sup>1</sup> C. S. Smith, Phys. Rev. **94**, 42 (1954).

<sup>2</sup> C. Herring, Bell System Tech. J. **34**, 237 (1955).

<sup>3</sup> E. N. Adams, Chicago Midway Laboratories Technical Report CML-TN-P8 (unpublished).

<sup>4</sup> C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

<sup>5</sup> R. W. Keyes, Phys. Rev. **100**, 1104 (1955).

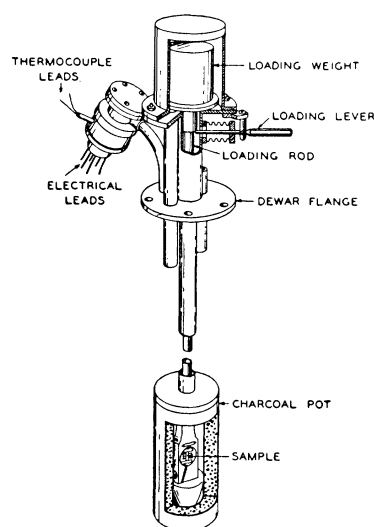


FIG. 1. Sample holder, showing method of loading the sample and the charcoal thermal mass.

vapor pressure thermometer and above 20°K with a copper-constantan thermocouple.

The piezoresistance effect was produced with compressive stress. The effect was taken to be positive when compression increased the resistance of the specimen. Thus, our effects are opposite in sign to the corresponding effects of Smith who used tension. The method of loading and unloading the sample is shown in Fig. 1. The loading rod was a thin-wall stainless steel tube terminated with a fiber plug for electrical insulation. To minimize thermal fluctuations, the rod was kept in contact with the sample and only the weight raised or lowered on the platform. The loading weight was varied from 100 to 1500 g to check the linearity of the effect with load. In general, the measurements were made using a load of 1000 g. This produced a stress of  $5.5 \times 10^7$  dynes/cm<sup>2</sup> on the samples where stress is parallel to current and  $1.0 \times 10^7$  dynes/cm<sup>2</sup> on the samples where

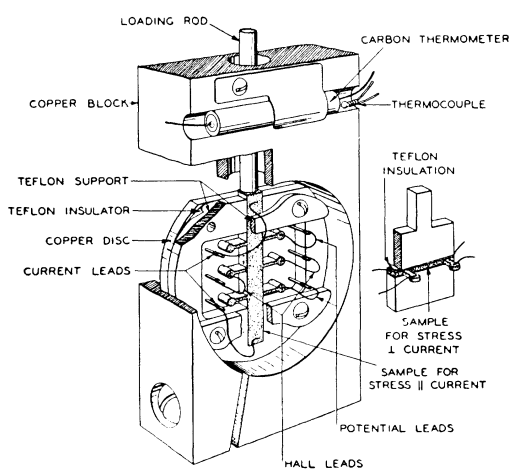


FIG. 2. Details of the mounting of the sample at the lower end of the sample holder.

stress is perpendicular to current. After each change in load sufficient time was allowed for the sample to regain thermal equilibrium. This was especially important when measuring the small piezoresistance effect since the effect itself was often of the same order as the difference between adiabatic and isothermal readings.

Sample shapes and the methods of mounting are shown in Fig. 2. Samples were oriented to within five minutes of arc on an x-ray goniometer modified for the purpose by W. L. Bond. All surfaces were initially sandblasted. Later on, a few samples were etched as a check on surface conduction. Lead wires were spot welded to the contact areas. The sample was loosely held in place by Teflon supports on a copper disk which was rotated and locked into place to align the sample with the loading rod.

When the sample resistance was below about  $10^5$  ohms, voltages were measured with a simple dc potentiometer circuit, a Leeds and Northrup microvolt amplifier as galvanometer with its output displayed on a strip chart recorder. Circuit unbalance produced by loading the sample was recorded on the chart. Measurements were made with constant sample current. This system was capable of detecting about  $\pm 0.01\%$  change in sample resistance when measuring the large effect and about  $\pm 0.002\%$  change when measuring the small effect. When sample resistance was above  $10^5$  ohms, a cathode-follower and high resistance galvanometer system were used in place of amplifier and recorder. Sample current could not be kept constant so change in current with loading was also measured. Contact resistance sometimes became serious and detector sensitivity was reduced. When contact resistance changed appreciably with load, results were discarded. Near the extreme of the high-resistance range the

TABLE I. Characteristics of the samples used.

Sample No.	Crystal No.	Major impurity	$N_D \times 10^{-13} \text{ cm}^{-3}$	$N_A \times 10^{-13} \text{ cm}^{-3}$	Orientation
<i>n</i> -type germanium					
1012	VIII-532	Sb	16.5	0.5	[110]
1046	Z-169-A	Sb	5.9	1.2	[110]
135	VIII-129	...	0.78	0.03	[110]
1008	VIII-343	As	9.6	0.3	[110]
1043	IV-194	As	170	2.0	[110]
1047	VIII-532	Sb	13.0	0.4	[100]
1048	Z-169-A	Sb	5.9	1.2	[100]
<i>p</i> -type germanium					
1051	Vac. 32	B	0.4	4.8	[110]
1052	ZL-510	In	1.6	2.3	[110]
1056	IV-319	Ga	...	150	[110]
1055	ZL-510	In	1.1	5.5	[100]
1057	IV-319	Ga	...	680	[100]
<i>n</i> -type silicon					
1049	VI-1273	P	13	...	[100]
1020	VI-1115D	P	15	1.5	[100]
1058	A-529	P	99	78	[100]
<i>p</i> -type silicon					
1053	A-388	B	30	60	[110]

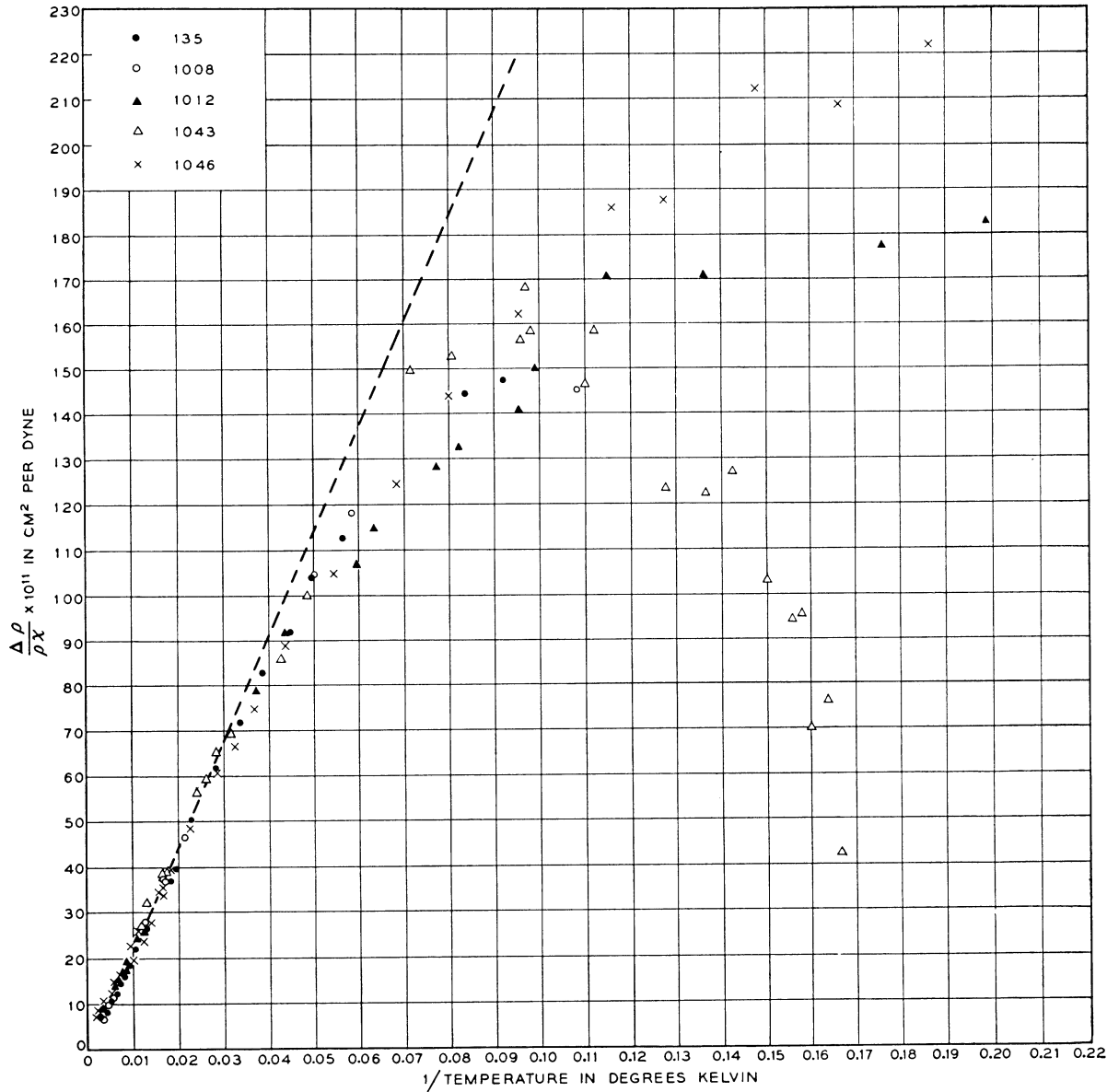


FIG. 3. Isothermal piezoresistance,  $\Delta\rho/\rho\chi = \frac{1}{2}(\Pi_{11} + \Pi_{12} + \Pi_{44})$ , as a function of reciprocal temperature for *n*-germanium oriented [110]. The line is that drawn in Fig. 4.

change in resistance was measured to about  $\pm 10\%$  with this system. The two systems were equivalent at a sample resistance around  $10^5$  ohms.

In general, Hall coefficient was measured using a magnetic field of 1000 oersteds. Linearity with electric and magnetic field was checked for an indication of surface and impurity band conductivity. The applied electric field in all measurements was kept below one volt per cm to avoid other nonlinear effects.

A summary of information concerning the samples used is given in Table I. For identification, the sample number and the number of the crystal from which it was cut are given. The identity of the major impurity,

donor concentration  $N_D$ , and acceptor concentration  $N_A$ , were determined from Hall data.

### 3. RESULTS

Some of the results which have been obtained are not reported in this paper because they were insufficiently precise for our purposes. For example, all data taken on silicon samples from crystals grown by the floating zone method have been discarded. The temperature dependence of the large piezoresistance effect of these samples differed greatly among samples and also differed from results obtained with crystals grown by the pulled method. This may have been due to the

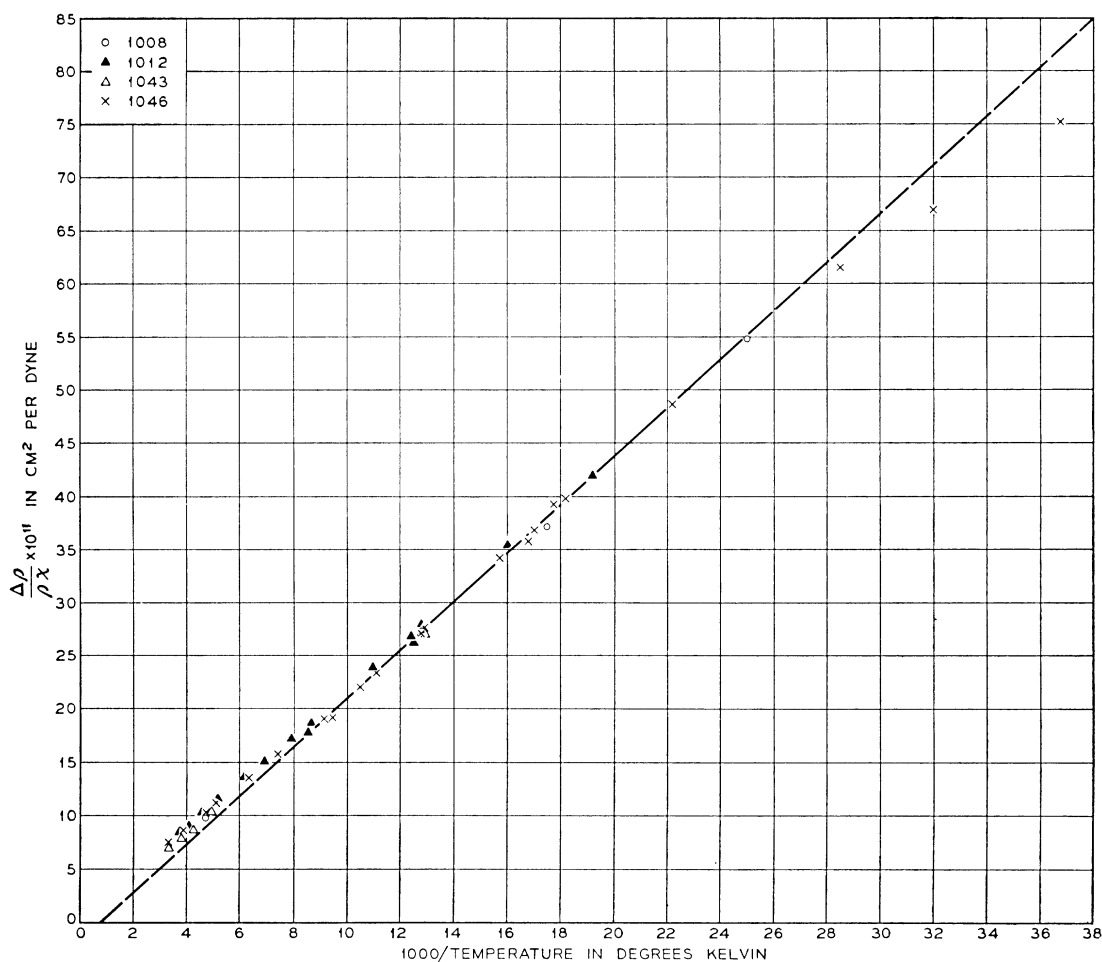


FIG. 4. An expanded plot of the high-temperature region of Fig. 3. The line was drawn to fit the data between 40° and 120°K.

unusually high concentration of dislocations in these floating zone silicon crystals. Results on samples where stress is perpendicular to current were not sufficiently reproducible. This may have been a result of the geometry of the samples (shown in Fig. 2) and the diffi-

culty of achieving a uniform stress over the large area of the sample. All of the piezoresistance data to follow were taken with longitudinal compression.

The piezoresistance effect is reported as fractional change in resistivity per unit stress. This was obtained in the case of the small effects from the measured fractional change in resistance by correcting for the dimensional change. This small correction was neglected in the case of the large effects.

### 3.1 Germanium Piezoresistance

General curves of the large piezoresistance effect in *n*-germanium are shown in Fig. 3. A linear dependence on reciprocal temperature is evident in the high-temperature portion of the curves and is shown in detail in Fig. 4. The straight lines represent the temperature dependence of piezoresistance due primarily to the population effect described in Sec. 4.1 below. The slight change of slope above 100°K, shown in Fig. 4, if real, is due to the onset of intervalley scattering (Sec. 4.1). The unexpectedly large departures from linearity at

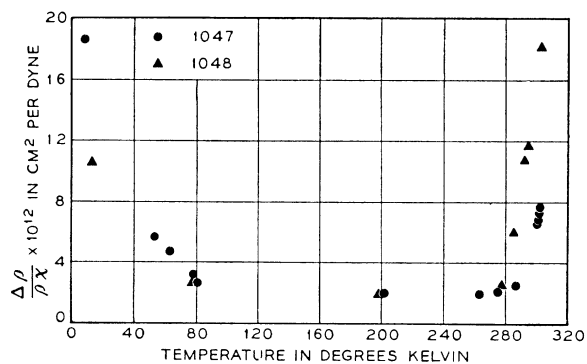


FIG. 5. Isothermal piezoresistance,  $\Delta\rho/\rho\chi = \Pi_{11}$ , as a function of temperature for *n*-germanium oriented [100].

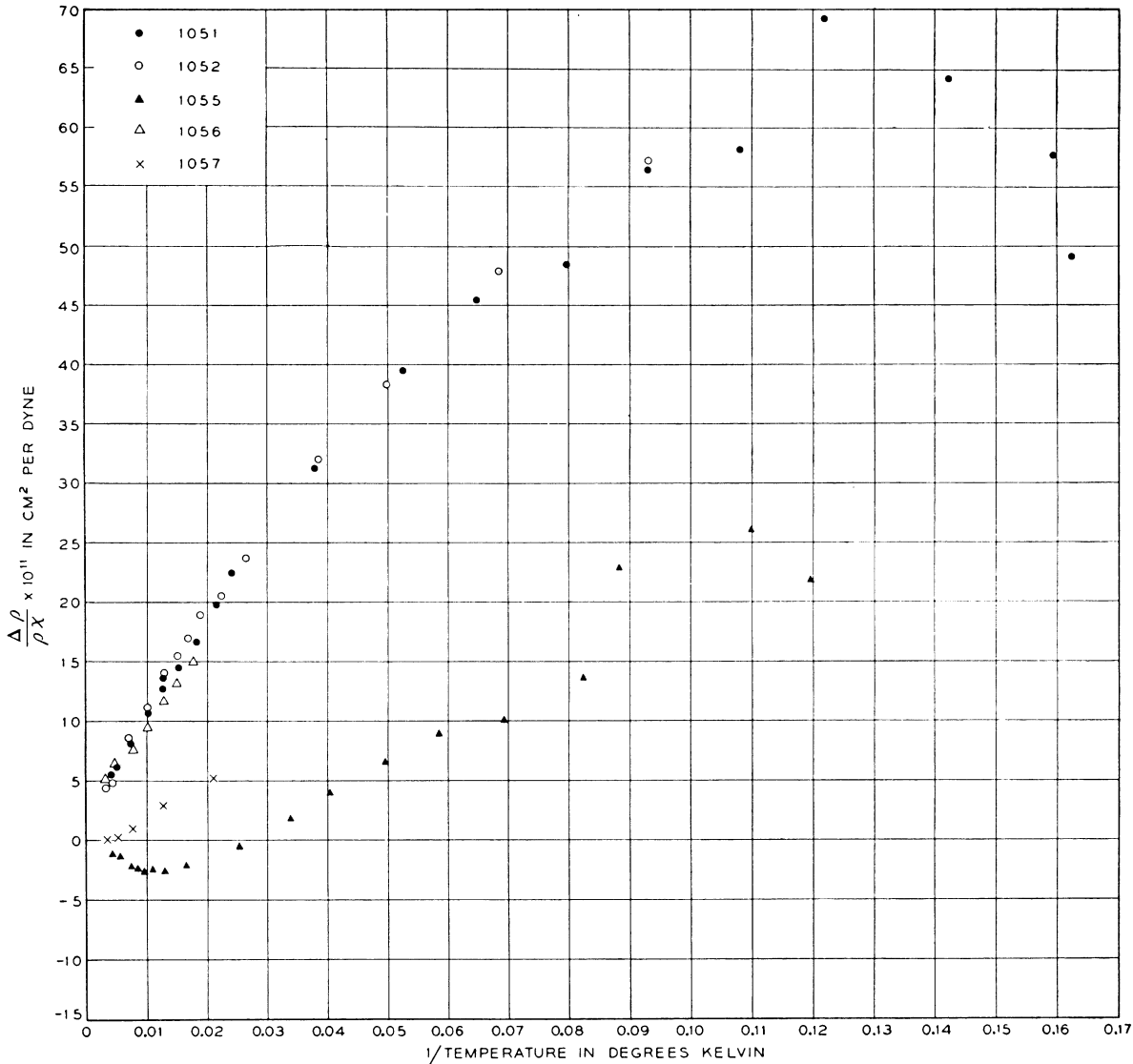


FIG. 6. Isothermal piezoresistance as a function of reciprocal temperature for *p* germanium. The upper set of data shows  $\Delta\rho/\rho\chi = \frac{1}{2}(\Pi_{11} + \Pi_{12} + \Pi_{44})$ , orientation [110]. The lower set of data shows  $\Delta\rho/\rho\chi = \Pi_{11}$ , orientation [100].

low temperatures are believed due to mechanisms other than impurity scattering (Sec. 4.3).

The small piezoresistance effect is represented by the central portion of the data in Fig. 5. The low-temperature rise is probably due to a small admixture of the large effect and the high-temperature rise to intrinsic conduction (Sec. 4.1). This measurement was particularly sensitive to sample misorientation but the agreement of the two samples suggests that this factor was below experimental error.

Data for two orientations of *p* germanium are shown in Fig. 6. Both orientations show a large effect with some tendency to depend linearly on reciprocal temperature.

### 3.2 Silicon Piezoresistance

Data for the large direction of *n* silicon and for *p* silicon are shown in Fig. 7 (crystals grown by the pull technique only). The large direction of the piezoresistance effect follows very well a linear dependence on reciprocal temperature, but the data are not precise enough to allow the intervalley scattering effect to be separated out. Two sets of data are shown for sample 1020. Actually four sets of data were taken on this sample, each successive set showing an additional decrease in the over-all piezoresistance. Sample 1058 represents a more recent crystal. It reproduces very well the earlier results and did not show a significant decrease in the piezoresistance effect with repeated

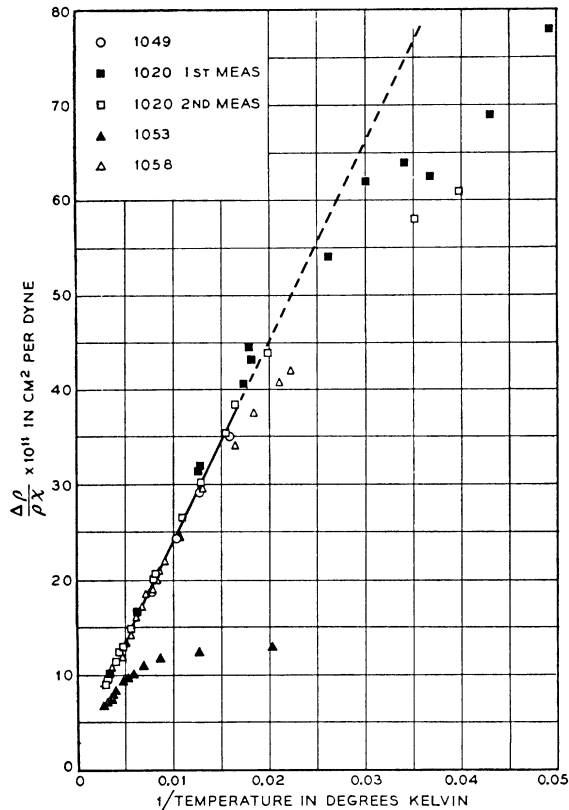


FIG. 7. Isothermal piezoresistance as a function of reciprocal temperature for silicon. The upper set of data shows  $\Delta\rho/\rho X = \Pi_{11}$  for  $n$ -silicon oriented [100]. The line was drawn to fit the data between 60° and 250°K. The lower set of data shows  $\Delta\rho/\rho X = \frac{1}{2}(\Pi_{11} + \Pi_{12} + \Pi_{44})$  for  $p$ -silicon oriented [110].

measurements at 50°K. The behavior of 1020 is unexplained, but may be connected with dissolved oxygen or dislocations, both of which are known to be present in amounts which vary from one crystal to another.

### 3.3 Hall Mobility

Mobilities for  $n$  germanium,  $p$  germanium, and  $n$  and  $p$  silicon are plotted in Figs. 8, 9, and 10, respectively. These results will be used to estimate the relative amounts of lattice and impurity scattering in the range above 10°K.

## 4. THEORY AND DISCUSSION

Since one of the principal reasons for undertaking these experiments was to obtain values of deformation potentials to use in the theory of mobility, we shall first discuss the relation of the results to the deformation-potential effect, the extent to which this relation may be influenced by impurity and intervalley scattering, and the evidence for the smallness of all other effects contributing to the piezoresistance. We shall see that useful conclusions about the nature of ionized-impurity

scattering can be drawn from the data. Our discussion for the  $p$ -type samples will include a description of the way in which deformation-potential effects influence the resistivity when the band edge is degenerate, as the existing literature<sup>6</sup> does not treat this explicitly.

Next, we shall discuss the departure from  $1/T$  behavior which all the data (shown in most detail in Fig. 3) manifest at temperatures low enough to freeze out most of the carriers onto the impurity centers. We have not been able to establish the cause of this with certainty; macroscopic and microscopic inhomogenities seem the most likely culprits. In any event, one can show that several conceivable causes are not adequate to explain the fall-off. This part of the discussion may help to draw attention to some of the difficulties besetting the interpretation of all kinds of electrical measurements on semiconductors at low temperature.

### 4.1 $N$ -Type Specimens, Donors Mostly Ionized

#### *Formulas for the Major Effects*

For a many-valley semiconductor such as  $n$ -type germanium or silicon, theory<sup>2-4</sup> predicts that the elastoresistance tensor should be a sum of several terms, of which the predominant one at moderately low temperatures is that due to the strain-induced change in the relative populations of the different valleys. This

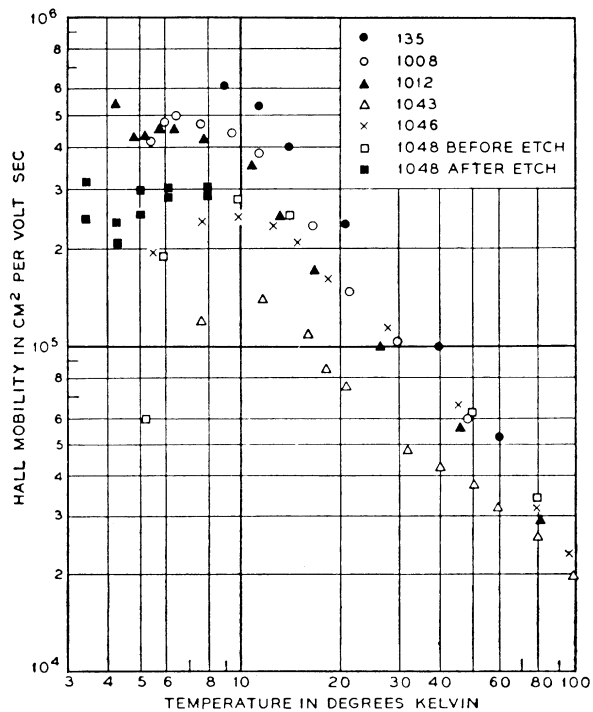


FIG. 8. Hall mobility as a function of temperature for  $n$  germanium.

<sup>6</sup> E. N. Adams, Phys. Rev. **96**, 803 (1954).

term has the form<sup>3</sup>

$$m_{44}^{(P)} = \frac{1}{9} \frac{\Xi_u (\mu_{11} - \mu_{\perp})}{kT \mu}, \quad (2)$$

$$m_{11}^{(P)} = m_{12}^{(P)} = 0, \quad (3)$$

for *n* germanium, and

$$m_{11}^{(P)} = \frac{2}{9} \frac{\Xi_u (\mu_{11} - \mu_{\perp})}{kT \mu}, \quad (4)$$

$$m_{44}^{(P)} = 0, \quad m_{12}^{(P)} = -\frac{1}{2} m_{11}^{(P)}, \quad (5)$$

for *n* silicon, where  $\mu_{11}$  and  $\mu_{\perp}$  are the mobilities of electrons in a single valley parallel and perpendicular, respectively, to the symmetry axis of the valley,  $\mu$  is the macroscopic mobility  $\frac{1}{3}(\mu_{11} + 2\mu_{\perp})$ , and  $\Xi_u$  is the deformation-potential constant for uniaxial shear, defined by the statement that  $\Xi_u u$  is the band-edge shift due to a stretch of amount  $u$  along the valley axis combined with a compression of amount  $\frac{1}{2}u$  in each of the two perpendicular directions. At high temperatures, where intervalley lattice scattering is important, a term  $m_{rs}^{(I)}$  must be added to  $m_{rs}^{(P)}$ , representing the effect of the deformation-potential shifts of energy on the probabilities for scattering from one valley to another.<sup>2</sup> This term goes as  $1/T$  at high  $T$ , but becomes exponentially negligible at low; explicit formulas for it are given in Appendix A. It obeys the same symmetry relations (3), (5), as  $m_{rs}^{(P)}$ .

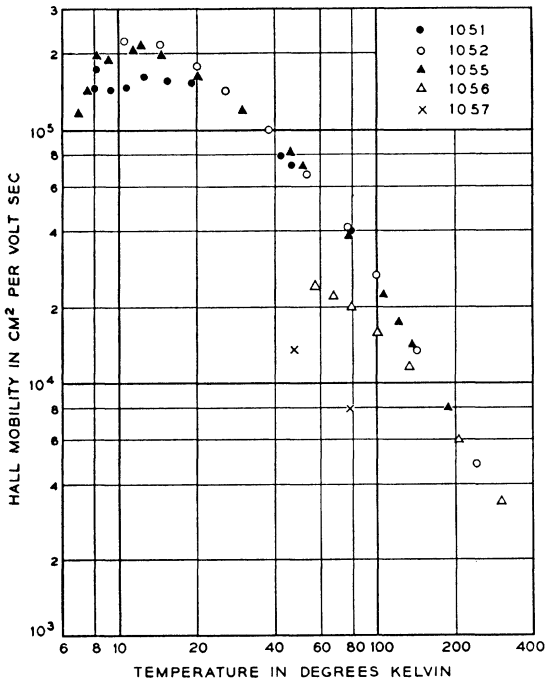


FIG. 9. Hall mobility as a function of temperature for *p* germanium.

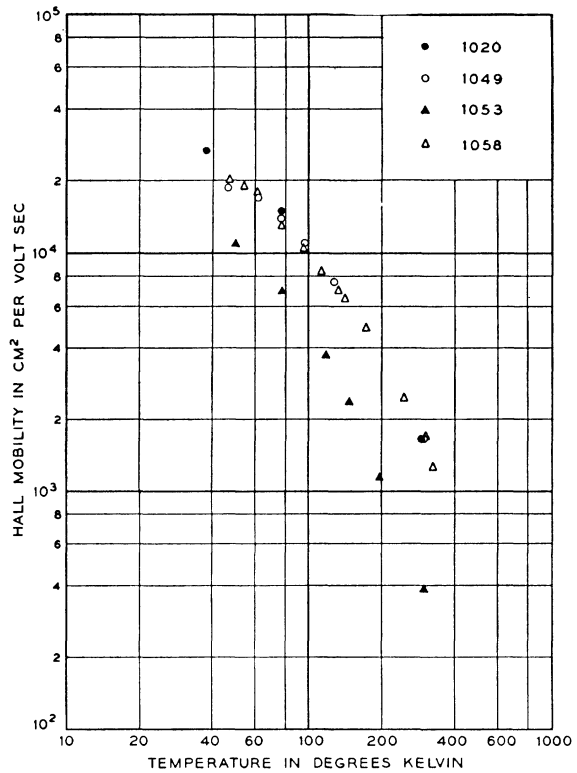


FIG. 10. Hall mobility as a function of temperature for *n* silicon (upper data) and *p* silicon (lower data).

*Discussion of the Minor Effects*

Additional contributions to the elastoresistance can arise from the alterations, due to strain, of the intrinsic band gap, the energies of impurity levels, the effective masses, and the matrix elements for scattering. For *n*-type germanium and silicon, at least, all these (except the first at high temperatures) should be small compared with the value at room temperature of the dominant term (2) or (4). However, these minor effects are not expected to have the symmetry property (3) or (5), so they can, and must, be responsible for the entire values of the minor components of  $m_{rs}$ . Over the temperature range in which pure acoustic scattering predominates, the effective-mass and matrix-element effects should be nearly independent of temperature. This expectation may be compared with the observations of Fig. 5 on [100]-oriented *n* germanium. Both specimens behave as expected,  $-\Pi_{11}$  decreasing rapidly as intrinsic carriers cease to be important just below room temperature, remaining nearly constant over quite a range of temperatures, and finally rising rapidly at low temperatures. The latter rise could well be due to a slight admixture of the large coefficient  $\Pi_{44}$  in the measured  $\partial\rho/\partial\chi$ , since  $\Pi_{44} \propto 1/T$ . Such an admixture would occur if anywhere in the sample the stress field and the current both departed from [100] orientation. Such departures are to be expected near the side arms.

TABLE II. Population-effect contributions to the isothermal piezoresistance constants of *n*-type germanium and silicon.

Substance and constant	Fitting range °K	Fitting line	Estimate of amount attributable to intervalley scattering contribution
Ge, $\frac{1}{2}(\Pi_{11} + \Pi_{12} + \Pi_{44})$ $m_{44}$	40°–120°	const – 22 600 × 10 <sup>-12</sup> /T cm <sup>2</sup> dyne <sup>-1</sup> const – 30 400/T <sup>a</sup>	None, in this range
Si, $\Pi_{11}$ $m_{11}$	60°–250°	const – 21 000 × 10 <sup>-12</sup> /T cm <sup>2</sup> dyne <sup>-1</sup> const – 21 500/T <sup>a</sup>	Slope of $\Pi_{11}^{(P)}$ perhaps 15% greater than that given

<sup>a</sup> Based on assumption that small components are independent of temperature.

Misorientation of the specimen may also contribute, especially if aided by inhomogeneities in conductivity. The side-arm effect predicts the sign of the low-temperature effect correctly, and the rise is in fact roughly like a  $1/T$  term. The other rise, near room temperature, is consistent with a roughly constant variation of electron mobility with strain, combined with an effect of strain on the intrinsic band gap. It is tempting to try to analyze the data for the two specimens simultaneously for the constants describing these two effects. However, to do this one must assume a value for the effect of strain on the mobility of holes, and this is not accurately known for material of this purity. About all that can be said is that the data are reasonably compatible with the known<sup>7</sup> change of conductivity under hydrostatic pressure, but suggest that either the change of electron mobility with strain is slightly larger at 300° than at 200°, or else the change of hole mobility is two or three times the change of electron mobility.

#### Numerical Values of the Population Effect

We shall now analyze the data on  $\Pi_{44}(\text{Ge})$  and  $\Pi_{11}(\text{Si})$  in a manner suggested by this evidence on the smallness and probable insensitivity to temperature of the elastoresistance contributions due to other than deformation-potential effects. If the contributions of these minor effects to these major components are comparably small and insensitive to temperature, a plot of the major component against  $1/T$  should, by (2) or (4), yield a straight line over any temperature range where intervalley scattering is negligible and the mobility anisotropy is constant, at least if any variation of  $\Xi_u$  with  $T$  in this range can be taken as linear in  $T$ . This is the reason for presenting the data of Figs. 3 and 7 in plots of this type. The slope of such a straight line portion measures the product of  $\Xi_u$  by the mobility anisotropy; since  $\mu_{\parallel} \ll \mu_{\perp}$  for *n* germanium and *n* silicon, the factor in parentheses in (2) and (4) is not very uncertain, being slightly  $> -\frac{3}{2}$ . The intercept of the straight portion of Fig. 3 or Fig. 7 should measure the effective-mass and matrix-element contributions to the component of  $\Pi$  in question, plus any effect from a temperature variation of  $\Xi_u$ , and a contribution from the intervalley effect discussed in the next paragraph, if this is appreciable over the fitting range. The straight lines drawn on Figs. 3 and 7 were fitted to the ranges

shown; they give the (uncorrected) population shift contributions listed in the next to the last column of Table II, and intercepts which are of the same order as the directly measured  $\Pi_{11}(\text{Ge})$  of Fig. 5 or the  $\Pi_{44}(\text{Si})$  of Smith.<sup>1</sup>

#### Intervalley Scattering Effect

Near room-temperature intervalley scattering should be considerable for *n* silicon, and perceptible, though not large, for *n* germanium. We therefore need to ask how much of the piezoresistance observed in this range should be attributed to the intervalley term  $m_{rs}^{(I)}$  mentioned above. Since this term, present at high temperature but not at low, should cause curvature in the plots of  $\Pi$  against  $1/T$ , we must decide whether the absence of perceptible curvature violates reasonable expectations, and, if not, whether the interpretation of the slopes of Figs. 3 and 7 in terms of Eqs. (2) and (4) needs to be modified because of the effect of the intervalley term. Although the theory of this term has been worked out,<sup>2</sup> quantitative predictions are hard to make because the parameters describing the intervalley scattering are not known, and because for any assumed set of parameters numerical integrations would be required. However, it is not hard to evaluate  $m_{rs}^{(I)}$  for the limiting cases of very small intervalley scattering (compared with intravalley) at any temperature, or of arbitrary intervalley scattering at high temperature. This is done in Appendix A. For germanium it appears that even if the departure of the mobility slope from  $\frac{3}{2}$  is attributed entirely to intervalley scattering, the intervalley contribution  $m_{44}^{(I)}$  for germanium at room temperature is only of the order of 15% of the population-shift term  $m_{44}^{(P)}$ . The curvature introduced into the plot of  $\rho^{-1}\partial\rho/\partial\chi$  against  $1/T$  by a term of this size could easily be overlooked; a straight line fitted to the data over a range like 80°–300°K would then have a slope a few percent lower than the slope of the population term alone. The present data show no curvature on the scale of Fig. 3, but the expanded plot of Fig. 4 shows that the points at higher temperatures appear to be perceptibly above the straight line fitted to the range 40°–120°K. This may well be due to the term  $m_{44}^{(I)}$ . For silicon  $m_{11}^{(I)}$  might be of the order of a third of  $m_{11}^{(P)}$ . This would probably not introduce perceptible curvature in the range 100°–300°, but would make the observed slope 15% or so lower than that of

<sup>7</sup> W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).



the population term. This rather uncertain correction is recorded in the last column of Table II.

### *Insensitivity to Impurity Scattering*

Figures 8 and 10 show evidence of appreciable impurity scattering below liquid air temperature for some of the *n*-germanium samples, and at rather higher temperatures for the *n*-silicon specimens. However, even a sizeable amount of impurity scattering seems to have very little effect on  $\Pi$ : the germanium specimen 1043, for example, has a mobility at 30° only about a third the ideal lattice scattering value, yet its ( $\Pi_{11} + \Pi_{12} + \Pi_{44}$ ) differs by no more than a few percent at most from that of the purer specimens. Although the fact that  $\mu_{\perp} \gg \mu_{\parallel}$  makes  $m_{44}$  insensitive to variations in the mobilities, a reduction of  $\mu_{\perp}$  by a factor 3 without a comparable reduction in  $\mu_{\parallel}$  would, by (2), reduce  $m_{44}$  by 15% or 20%. Thus we may conclude that a moderate amount of ionized impurity scattering reduces  $\mu_{\parallel}$  and  $\mu_{\perp}$  in comparable ratios, or else reduces  $\mu_{\parallel}$  more. This is a significant conclusion, as it has not been obvious *a priori* that this should be so.

## 4.2 P-Type Specimens, Acceptors Mostly Ionized

### *Generality of the Relation $\Pi \propto T^{-1}$*

For a degenerate band structure, just as for a many-valley model, we expect the shifts  $\delta\epsilon(\mathbf{K})$  of the electronic energy levels with strain to give elasto-resistance contributions of order  $\delta\epsilon/kT$ , while all other effects should give much smaller contributions. The situation is now more complicated, however, since a shearing strain will in general lift the degeneracy of the band edge and warp the energy surfaces.<sup>6</sup> Through these effects the strain influences the current not only by changing the equilibrium populations of the states of the carriers, but also by changing the group velocities and the wave functions which enter into the matrix elements for scattering.

We can nevertheless show that for a large class of cases the predominant effects go as  $T^{-1}$ . Let us assume that for any small strain  $u$  the dependence of energy on wave vector  $\mathbf{K}$  in each band is of the form

$$\epsilon(\mathbf{K}, u) = \alpha(\text{direction})K^2 + u\beta(\text{direction}). \quad (6)$$

$\alpha$  and  $\beta$  being unspecified functions of the direction of  $\mathbf{K}$ , and independent of temperature. Let us also assume that the squared matrix element for scattering is of the form

$$|M(\mathbf{K}, \mathbf{K}')|^2 = F(T)[G_0(\text{directions}) + (u/K^2)G_1(\text{directions})], \quad (7)$$

where  $G_0, G_1$  are functions of the directions of  $\mathbf{K}, \mathbf{K}'$ , and  $\mathbf{K} - \mathbf{K}'$ , and of the bands in which states  $\mathbf{K}, \mathbf{K}'$  lie. The dependence of  $u/K^2$  is of the proper form to take account of mixing of the wave functions of the degenerate bands by the strain. The assumptions (6)

and (7) should be good approximations if the width  $kT$  of the occupied energy range is much less than the separation of the degenerate band edge in question from other bands, if the effective-mass constants are temperature-independent, and provided  $M(\mathbf{K}, \mathbf{K}')$  is dominated by acoustic scattering. For very small  $K$ , of course,  $\alpha K^2$  and  $u\beta$  will become comparable, and (6) and (7) will break down; however, the number of states in this range is of order  $u^3$ , hence too small to affect the first derivative of conductivity with respect to  $u$ .

Now consider the Boltzmann transport equation, an integral equation for the first-order change in the distribution function due to an applied electric field. The kernel is the scattering function  $S(\mathbf{K} \rightarrow \mathbf{K}')$ , while the inhomogeneous term is proportional to the gradient of the equilibrium distribution function  $f^{(0)}$ . For Maxwellian statistics let

$$\tilde{f}^{(0)} \equiv f^{(0)} \exp(-\epsilon_F/kT) = \exp(-\epsilon/kT).$$

Then for any  $\lambda$  our assumptions give the scaling laws

$$\tilde{f}^{(0)}(\mathbf{K}; u, T) = \tilde{f}^{(0)}(\lambda\mathbf{K}; \lambda^2 u, \lambda^2 T), \quad (8)$$

$$S(\mathbf{K} \rightarrow \mathbf{K}'; u, T) = BS(\lambda\mathbf{K} \rightarrow \lambda\mathbf{K}'; \lambda^2 u, \lambda^2 T), \quad (9)$$

where  $B$  depends on  $T$  and  $\lambda^2 T$ , but not on  $u, \mathbf{K}, \mathbf{K}'$ . If  $u$  is a shearing strain, so that  $\partial\epsilon_F/\partial u = 0$ , both the kernel and the inhomogeneous term in the transport equation for strain  $\lambda^2 u$  at temperature  $\lambda^2 T$  will scale from those for  $u, T$  with factors that depend on the temperatures but not on  $u$ . Therefore a strain  $\lambda^2 u$  produces as much fractional change of current at temperature  $\lambda^2 T$  as does a strain  $u$  at temperature  $T$ , i.e.,

$$\text{elasto-resistance coeff. for shear} \propto T^{-1}. \quad (10)$$

The most important causes for departures from (10) are, as we shall see, impurity and optical mode scattering, proximity of other bands which cause departures from the parabolic law (6), and, possibly, temperature-dependence of the masses.

### *Data for *p* Germanium: Sensitivity to Impurity Scattering*

Whereas for *n* germanium and *n* silicon the symmetry of the band-edge points causes the population effect from certain types of shear to vanish, there are no such symmetry restrictions on the major elasto-resistance coefficients for *p* germanium. The fact that Smith<sup>1</sup> found  $\frac{1}{2}(m_{11} - m_{12}) \ll m_{44}$  at room temperature has therefore occasioned comment.<sup>6</sup> The data of Fig. 6 show that there are indeed two piezoresistance coefficients which, as  $T$  decreases, become much larger than anything that could be attributed to the "minor" effects. With allowance for impurity scattering (see below) and for partial cancellation of the major and minor effects near room temperature, the difference in the magnitudes of the two coefficients does not seem

preposterously large. Thus ideally one should be able to extract from piezoresistance data the values of two deformation-potential constants. However, to do this even with ideal data one would need a more detailed theory than has yet been worked out.

Actually, as Fig. 6 shows,  $T^{-1}$  behavior does not hold very well, but one can argue that this departure from ideality is probably to be expected. There are at least three effects which can make the elasto-resistance more sensitive to impurity scattering and optical mode scattering in  $p$ -type than in  $n$ -type material. The first of these is that the piezoresistance of light and heavy holes may be quite different, and the light holes are notoriously sensitive to impurity scattering. The second point is that, according to (6), the anisotropy introduced into the energy surfaces by strain becomes larger and larger the lower the kinetic energy  $\Delta\epsilon$  of the holes. The effect of strain on certain components of group velocity therefore gets very large at small  $\Delta\epsilon$ , and so the low-energy holes may contribute a very large share of the elasto-resistance. But it is the low-energy holes that are most susceptible to impurity scattering. The third effect is that the strain may also alter the anisotropy of the scattering processes, and may alter it differently depending on the relative amounts of different kinds of scattering.

The room-temperature data of Smith<sup>1</sup> seem to confirm this expected sensitivity to impurity scattering, as they show a marked dependence of  $\Pi_{11}-\Pi_{12}$  on purity. For a further confirmation the measurements on specimen 1057, shown in Fig. 6, were taken. The difference between these points and those for the purer specimens is striking, and contrasts with the almost imperceptible difference between specimen 1043 and the purer specimens in Fig. 3.

Some measurements of the effect of a magnetic field were made on sample 1055 at 78°K to test the speculation that the sensitivity to impurity content arises from the current contribution of the light holes, or from that of very low-energy holes. A reversal of the sign of  $\partial\rho/\partial\chi$  was found in a field of only 250 oersteds; this seems to confirm the speculation.

#### *Data for p Silicon*

For silicon it is known that the spin-orbit splitting separating the two levels at  $K=0$  is no more than, and probably of the order of, 0.03 eV.<sup>8</sup> Thus equations such as (6) to (10) should not be applicable above liquid air temperature. Although the points of Fig. 7 fit a straight line fairly well down to 200° or 150°K, this rectilinearity must be regarded as accidental, and the line is doubtless not related in any very simple way to any single constant of the material. Near and below liquid air temperature, on the other hand, impurity scattering is surely a major factor, so there is no part of the tem-

perature range where there seems to be much hope of interpreting the data quantitatively.

#### **4.3 Apparent Decrease of $\Pi$ as Carriers Freeze Out**

All the data of Figs. 3, 6, and 7 show that for each material the large piezoresistance coefficient fails to increase as rapidly as  $T^{-1}$  when the temperature is lowered into the range where most of the carriers are freezing out onto donors and acceptors. Simultaneously, the fluctuations from specimen to specimen increase greatly: for example, in Fig. 3 the apparent  $\Pi_{44}$ 's of different  $n$ -germanium specimens agree to within a few percent above 20°K, but range over 15% or so at 10°, and much more at lower temperatures. For the  $p$  germanium and the  $n$  silicon it is hard to exclude impurity scattering as a possible cause of this behavior, though one is struck by the fact that  $\Pi$  is always smaller than the extrapolation from higher temperatures. For  $n$  germanium, however, we shall show that impurity scattering is not responsible, and that some other cause, probably associated with inhomogeneities, must be invoked. This cause might well affect the  $p$ -type specimens the same way.

#### *Arguments Against Attributing the Anomalies to Impurity Scattering*

In the discussion of the higher temperature data for the  $n$ -type material we have already noted that, for these, the piezoresistance is not greatly affected by ionized-impurity scattering, even when this is sufficient to reduce the mobility by a factor two or three. So prospects are not bright for accounting for the anomalies in this way; we shall try to tighten the argument in several ways.

Equations (2) to (5) should represent the dominant population-effect contribution to the elasto-resistance whenever the specimen can be considered homogeneous with its current carried by electrons in the conduction band and limited by scattering processes describable in terms of transition probabilities. Our present argument can be characterized as a proof that no reasonable picture of this sort can account for the fall-off from  $T^{-1}$  behavior. We note first that because of the smallness of the energies of the phonons active in lattice scattering, there cannot be any very great change in the anisotropy of acoustic lattice scattering between 30° and 10°, or any very great departure from the  $T^{-3/2}$  law of mobility. Thus only impurity scattering or a temperature variation of  $\Xi_u$  could cause the values of (2) or (4) to depart seriously from  $T^{-1}$  behavior. But impurity scattering can only reduce  $\mu_{11}$  and  $\mu_{\perp}$  below their lattice-scattering values; it cannot increase either. The greatest possible decrease in  $m_{44}^{(P)}$ , for a given decrease in  $\mu$ , occurs when the decrease in  $\mu$  is due entirely to a decrease in  $\mu_{\perp}$ , since  $\mu_{\perp} \gg \mu_{11}$ . The purer  $n$ -germanium specimens show a moderate reduction of mobility below

<sup>8</sup> A. H. Kahn, Phys. Rev. **97**, 1467 (1954).

that due to acoustic scattering, but as is shown in Appendix B, this reduction is by no means sufficient to account for the reduction of  $m_{44}$ , even in the unlikely extreme that all the reduction is in  $\mu_{11}$ .

The actual effect of impurity scattering must fall far short of this extreme, since, as we have noted above, even a sizeable amount of impurity scattering has little effect at slightly higher temperatures. For example, the mobility reduction for specimen 1043 at 30°K is of the same order as, or greater than, that of any of the purer specimens at 10°, yet the piezoresistance of 1043 is, if anything, a few percent greater than that of the others. The two cases should be truly comparable, as it can be verified (Appendix B) that in both cases ionized impurity scattering far outweighs scattering by neutral impurities.

*Absence of an Appreciable Effect of Strain on the Degree of Ionization of the Donors*

The fact that departures from  $T^{-1}$  behavior occur in the very range of temperatures where the carriers are freezing out onto impurity centers suggests the possibility of a strain-induced change in the degree of ionization. For very small strains no appreciable change of this sort is to be expected, however, since to the first order in the strain only the volume dilation can affect the degree of ionization, and since this volume effect on the ionization energy would probably be small, of the same order as the change of the effective mass with compression. Observation also suggests this conclusion, since the volume effect should be the same for any orientation of the specimen whereas the total  $\Pi_{11}$  of Fig. 5 is some tens of times smaller than the departure from linearity in Fig. 3. As an additional check, Hall measurements with and without load were compared for sample 1012, a well-behaved germanium specimen. The change in Hall voltage with a 1000-g load was found to be less than 0.5% at 10°K.

Shear can affect the degree of ionization to the second order in the strain. However, the data shown in Fig. 3 were linear in the load up to the maximum of  $7.9 \times 10^7$  dynes/cm<sup>2</sup>, so the nonlinear range has evidently not been reached.

*Difficulties with Other Explanations for the Fall-off Which Assume Homogeneous Conduction by Free Carriers*

We have by now ruled out the possibility of attributing most of the anomalies to the population effect, if the deformation-potential constant  $\Xi_u$  is temperature-independent. We have now to consider whether the anomalies could be due to temperature dependence of  $\Xi_u$ , to an intervalley scattering effect, or to the "minor" contributions to the piezoresistance. The latter are presumably of the order of a few times  $10^{-12}$  cm<sup>2</sup>/degree, while the anomalies in Fig. 3 and the other figures are of the order of many hundreds of the same units. Even if the low-temperature rise in the  $\Pi_{11}$  of Fig. 5 were

considered to be real, the indicated magnitude of the "minor" contributions would still be far too small to account for the anomalies. As for intervalley scattering, intervalley lattice scattering is certainly negligible in the present temperature range, and intervalley impurity scattering would surely be a very small fraction of the total impurity scattering, hence would affect  $\Pi$  by a percentage enormously less than the reduction of the mobility by all kinds of impurity scattering together.

A temperature variation of  $\Xi_u$  could arise either from thermal expansion or from a strain-dependence of the thermal shift of the band edge which is known to be produced by the electron-phonon interaction.<sup>9</sup> However, both these effects should give  $d\Xi_u/dT=0$  at  $T=0$ , and a consideration of their probable orders of magnitude suggests that only a small fraction of the piezoresistance anomaly could be attributed to these effects. Note that any large temperature dependence of  $\Xi_u$  would probably cause the mobility slope to depart greatly from the ideal value  $-\frac{3}{2}$ .

None of these alternative mechanisms which we have just rejected would account for the variability of the piezoresistance from specimen to specimen.

*Short-Circuiting by Other Conduction Mechanisms Above 10°K*

Impurity band, dislocation, or surface conduction could modify the piezoresistance by short-circuiting the normal free-carrier conduction mechanism; such effects would vary from specimen to specimen. However, we consider it unlikely that they were responsible for the piezoresistance anomalies of germanium above 10°K. Impurity band conduction at such temperatures seems out of the question for samples as pure as most of the ones used; moreover, there is no sign of it in the behavior of the Hall mobility. Etching the surfaces of some of the specimens had almost no effect on  $\Pi$  above 10°, though as we have mentioned earlier, there was evidence in some cases of surface conduction at lower temperatures. In general, any parallel conduction mechanism would be expected to have an activation energy very different from that of the donors, and so to come in catastrophically as the temperature is lowered. The anomalies of Fig. 3 do not do this.

*Possible Effects of Macroscopic Inhomogeneities*

Inhomogeneities, which we are now led to consider, can be present on any scale. We shall apply the term "macroscopic" to inhomogeneities whose scale is large compared with a Debye screening length. Note that since local alterations in the proportions of charged and neutral centers can contribute to screening effects, this length does not usually get very large, even at low temperatures. The presence of such inhomogeneities

<sup>9</sup> Fan, Shepard, and Spitzer, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. Breckenridge (John Wiley and Sons, Inc., New York, 1956).

modifies the distributions of current  $\mathbf{j}$  and field  $\mathbf{E}$  in a way that is determined by the classical equations  $\nabla \times \mathbf{E} = \nabla \cdot \mathbf{j} = 0$ ,  $\mathbf{j} = \sigma \cdot \mathbf{E}$ , with  $\sigma$  (which in the presence of strain or of a magnetic field is in general a tensor) varying from point to point. What we wish to estimate here is how large an effect reasonable kinds of macroscopic inhomogeneities can have on the apparent piezoresistance, subject to the condition that the apparent Hall mobility not be reduced below ideal mobility by more than a moderate factor. The estimate will depend somewhat on whether the variation of  $\sigma$  is due to variation of carrier concentration  $n$  or of local mobility  $\mu_H$  or both; since  $n$  is likely to fluctuate more than  $\mu_H$ , we shall discuss only the case of variable  $n$ , constant  $\mu_H$ .

First of all, we may note that the only inhomogeneities which will modify  $\Pi$  are those that cause the local  $\mathbf{j}$  to make an angle with the specimen axis. Thus we get little effect from fluctuations of  $n$  in distances along the length of the specimen which are several times the diameter, or from a variation of  $n$  with depth below the surface. Thus it is not unreasonable to focus attention on inhomogeneities which, though macroscopic, are on a scale rather smaller than the size of the specimen. If the fluctuations in  $\sigma$  due to such inhomogeneities are small, their effect on the measured conductivity, Hall effect, piezoresistance, etc., can be calculated without further assumptions by the device of developing all field quantities into Fourier series.<sup>10</sup> If the fluctuations are statistically isotropic, it turns out<sup>10</sup> that for a specimen oriented in a direction of maximum longitudinal piezoresistance the apparent piezoresistance  $\Pi_{ap}$  and the apparent Hall mobility  $\mu_{Hap}$  are related by

$$\frac{\Pi_{ap}}{\Pi} = \frac{2}{5} + \frac{3}{5} \frac{\mu_{Hap}}{\mu_H}, \quad (11)$$

where  $\Pi$  and  $\mu_H$  characterize any homogeneous region of the given material. This relation contrasts with the effect of impurity scattering discussed above and in Appendix B, where for nearly ideal material the maximum possible fractional reduction of  $\Pi$  below the ideal value was found to be only a fraction  $3\mu_{II}/2(\mu_{\perp} - \mu_{II})$  of the reduction in  $\mu$ , instead of  $\frac{3}{5}$  as in (11).

Although (11) was derived only for the case of infinitesimal fluctuations, a rough consideration of some cases involving larger fluctuations suggests in most cases it is not far from the truth. Moreover, our main interest is in temperatures where the piezoresistance anomalies have just begun, so that the fluctuations, if such be the cause, are small. Comparison of (11) with the data of Figs. 3 and 8 suggests that macroscopic inhomogeneities could well have been great enough to account for a large part of the piezoresistance anomalies below 20°K, though perhaps not for all, since the ratio  $\mu_{Hap}/\mu_H$  in (11) must be taken appreciably nearer

unity than the ratio  $\mu_{Hap}/\mu_{HA}$  of measured to ideal lattice-scattering mobility.

#### *Microscopic Inhomogeneities*

In the temperature range where the piezoresistance anomalies occur the mean free path of the carriers is long, and one might suppose that any effects of inhomogeneities on a scale smaller than the screening length would be included under the heading of impurity scattering, which we have discussed above. This is not quite true, however. For in the usual use of impurity scattering in transport theory—and in our use of it above—it is assumed that the rate of change of the velocity distribution due to scattering is determined by the velocity distribution alone. This is only true if the distributions of the carriers in space and in velocity are independent, i.e., if carriers of a given velocity are exposed to a random sampling of the scattering centers as they move along. This is usually a good approximation at high temperatures, but fails when a sizable part of the conduction is by carriers whose kinetic energies are less than the mean fluctuation of potential energy over a mean free path.

A complete transport theory valid under the conditions just mentioned has yet to be worked out. However, it is possible to calculate some properties of an extreme case, namely, the case of electrons in a number of potential valleys of depth  $\gg kT$ , which percolate from valley to valley by thermionic emission over the passes, and which have a mean free path for lattice scattering rather larger than the dimensions of the valleys. For this case, which is certainly far more extreme than the situation which obtains for germanium at 10°K, it appears that one can get a reduction of the piezoresistance to perhaps a third of the ideal value, because of the random orientations of the potential passes over which the electrons jump. Thus it is conceivable that departures from the usual model of impurity scattering may contribute to the lowering of the piezoresistance, especially at temperatures in the helium range.

#### *Short-Circuiting Mechanisms below 10°K*

The dislocation density in all samples is considered too low to be serious, so we shall consider briefly the evidence that impurity band and surface conduction short-circuited the normal conduction mechanism in some samples and produced the anomalies observed below 10°K in germanium.

Our experience and that of others<sup>11</sup> indicates that appreciable impurity band conduction will be found below 10°K in samples containing  $10^{15}$  to  $10^{16}$  cm<sup>-3</sup> donors and acceptors. Sample 1043 contains  $1.72 \times 10^{15}$  cm<sup>-3</sup> donors and acceptors and shows in Fig. 8 a rapid mobility decrease below 10°K which is typical for conduction in an impurity band in parallel with the

<sup>10</sup> C. Herring (to be published).

<sup>11</sup> H. Fritzsche, Phys. Rev. **99**, 406 (1955).

conduction band. This probably accounts for most of the rapid drop in piezoresistance below 10°K shown for 1043 in Fig. 3. The result is not due to surface conduction since etching the sample caused no change in the low-temperature mobility or piezoresistance.

Occasionally a high-purity germanium sample also showed a rapid decrease in mobility and piezoresistance below 10°K. In these instances the low-temperature conductivity was dependent upon applied electric fields for fields as low as 0.01 volt/cm. After etching the sample, these effects were eliminated and the mobility and piezoresistance remained high to the low-temperature limit of measurement. As an example of this behavior, the mobility of sample 1048 measured before and after etching is shown in Fig. 8. The occasional event of surface conduction is hard to explain since all samples were prepared using the same procedure.

Two sets of points are shown for the low-temperature mobility of 1048 after etching which represent an increase in mobility with an increase in electric field. This effect is probably due to inhomogeneities in the body of the sample.

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#### APPENDIX A. INTERVALLEY SCATTERING

We shall try to evaluate explicitly the expression for the contribution  $m_{rs}^{(I)}$  of the intervalley scattering effect to the elastoresistance tensor, for two limiting cases. We start with the general expression for  $m_{rs}^{(I)}$  for a cubic semiconductor with valleys on [100] or [111] axes of the Brillouin zone, and for which the scattering processes are describable by a relaxation time dependent on energy only. This expression is,<sup>2</sup> with  $r \rightarrow \mu\nu$ ,  $s \rightarrow \alpha\beta$  ( $\mu, \nu, \alpha, \beta = 1$  to 3):

$$m_{\mu\nu\alpha\beta}^{(I)} = -\Xi_u N_V \times \left\langle \frac{\langle \Delta\epsilon \partial\tau^{(i)}/\partial\epsilon^{(i)} \rangle}{\langle \epsilon\tau \rangle} \frac{K_\mu^{(i)} K_\nu^{(i)}}{K^{(i)2}} \frac{K_\alpha^{(j)} K_\beta^{(j)}}{K^{(j)2}} \right\rangle_{i,j} \times \left( \frac{\mu_{11} - \mu_{12}}{\mu} \right), \quad (\text{A1})$$

where  $\Xi_u$  is the deformation potential constant defined in connection with Eqs. (2) to (5),  $N_V$  is the number of valleys,  $\Delta\epsilon$  is the energy of the electrons or holes relative to the band edge,  $\partial\tau^{(i)}/\partial\epsilon^{(i)}$  is the change in the relaxation time of carriers in valley  $i$  due to a shift of the band edge energy of valley  $j$ , and the  $\mathbf{K}^{(i)}$  are the wave vectors of the valley centers. The smaller angular brackets denote Maxwellian averages, and the outer ones averages over all valleys  $i$  and  $j$ .

For  $n$  germanium there are presumably four valleys, whose  $\mathbf{K}^{(i)}$  point in the tetrahedral directions. (For band-edge points on the boundary of the Brillouin zone the valleys  $\mathbf{K}^{(i)}$  and  $-\mathbf{K}^{(i)}$ , or  $i$  and  $-i$  for short, are the same.) Therefore, from symmetry

$$\text{Ge: } \partial\tau^{(i)}/\partial\epsilon^{(i)} = f(\Delta\epsilon) \quad \text{if } j \neq i \\ = -3f(\Delta\epsilon) \quad \text{if } j = i. \quad (\text{A2})$$

For  $n$ -silicon these are six band edge points, on [100] axes of the Brillouin zone. We have

$$\text{Si: } \partial\tau^{(i)}/\partial\epsilon^{(i)} = f(\Delta\epsilon) \quad \text{if } j \neq i \text{ or } -i \\ = g(\Delta\epsilon) \quad \text{if } j = -i \\ = -4f(\Delta\epsilon) - g(\Delta\epsilon) \quad \text{if } j = i. \quad (\text{A3})$$

Inserting these forms into (A1) and evaluating the averages on  $i$  and  $j$ , we find for the ratios of (A1) to (2) or (4)<sup>12</sup>:

$$\text{Ge: } m_{44}^{(I)}/m_{44}^{(P)} = 4kT \langle \Delta\epsilon f \rangle / \langle \Delta\epsilon\tau \rangle, \quad (\text{A4})$$

$$\text{Si: } m_{11}^{(I)}/m_{11}^{(P)} = 6kT \langle \Delta\epsilon f \rangle / \langle \Delta\epsilon\tau \rangle. \quad (\text{A5})$$

Note that the  $g$  term in (A3) makes no direct contribution to the elastoresistance, since valleys  $i$  and  $-i$  must always undergo the same energy shift with strain.

Although it would not be difficult to evaluate  $\langle \Delta\epsilon f \rangle$  and  $\langle \Delta\epsilon\tau \rangle$  numerically for any simple model of intervalley scattering, we shall be content here to evaluate (A4) or (A5) for several limiting cases. These expressions are functions of the temperature  $T$  and the ratio  $w_2/w_1$  of the coupling constant for intervalley scattering to that for intravalley. [We use the notation of reference 2 and for the moment assume  $g=0$  in (A3).] When  $T$  is small compared with the characteristic temperature  $\hbar\omega/k$  of the intervalley phonons, they go exponentially to zero, while at high  $T$  they approach limiting values. For  $T \gg \hbar\omega/k$  both inter- and intravalley scattering probabilities can be taken proportional to  $\Delta\epsilon^2$ , and the ratio of the former to the latter is  $2w_2/w_1$ . We find therefore, in the absence of impurity and optical mode scattering,

$$f \sim \frac{\gamma T}{\Delta\epsilon} \left[ \frac{w_2/w_1}{(2w_2/w_1) + 1} \right], \quad (\text{A6})$$

with  $\gamma = \frac{1}{3}$  for germanium,  $\frac{1}{4}$  for silicon. Thus, at high  $T$ ,

$$\text{Ge: } \frac{m_{44}^{(I)}}{m_{44}^{(P)}} \sim \frac{4}{3} \left[ \frac{w_2/w_1}{(2w_2/w_1) + 1} \right] < \frac{2}{3}, \quad (\text{A7})$$

$$\text{Si: } \frac{m_{11}^{(I)}}{m_{11}^{(P)}} \sim \frac{3}{2} \left[ \frac{w_2/w_1}{(2w_2/w_1) + 1} \right] < \frac{3}{4}. \quad (\text{A8})$$

If  $g \neq 0$  in (A3), the value of (A8) will of course be less, but the upper limit will be the same. The effect of scattering by optical modes on (A7) and (A8) is similar.

<sup>12</sup> Equivalent formulas have been obtained by R. W. Keyes, Phys. Rev. **103**, 1240 (1956). We are indebted to Dr. Keyes for communicating his results to us in advance of their publication.

In general, we can write

$$1/\tau^{(i)} = W_{ii} + \sum_{j \neq i} (W_{ij}^{(a)} + W_{ij}^{(e)}), \quad (\text{A9})$$

where  $W_{ii}$  is the intravalley scattering probability and  $W_{ij}^{(a)}, W_{ij}^{(e)}$  are the probabilities for absorption and emission, respectively, of an intervalley phonon of the type to connect valleys  $i$  and  $j$ ; the second  $\sum$  denotes a summation over different branches of the phonon spectrum. Changing the energy of the  $j$ th band-edge point simply shifts the function  $(W_{ij}^{(a)} + W_{ij}^{(e)})$  along the energy scale. Thus

$$f = -\tau^2 [\partial W^{(i)} / \partial \epsilon^{(j)}], \quad (\text{A10})$$

where  $W^{(i)}$  is the summation in (A9). If  $w_2/w_1$  is small,  $W^{(i)}$  is small compared with the first term, and if the first term represents purely acoustic scattering, so that

$$\tau^{-1} \approx W_{ii} \propto \Delta \epsilon^{\frac{1}{2}},$$

then

$$\langle \Delta \epsilon f \rangle = \gamma \left[ (kT)^{-1} - (2\Delta \epsilon)^{-1} \right] W^{(i)} (\Delta \epsilon \tau^2) + O(W^{(i)2}), \quad (\text{A11})$$

where, as before,  $\gamma = \frac{1}{3}$  (Ge) or  $\frac{1}{4}$  (Si), and  $(\Delta \epsilon \tau^2)$  is, by hypothesis, a constant. Explicit integration shows that when each  $W_{ij}^{(a,e)}$  is of the form

$$W_{ij}^{(a)} = w_2 \left[ \frac{\Delta \epsilon}{\hbar \omega} + 1 \right]^{\frac{1}{2}} \left[ \exp(\hbar \omega / kT) - 1 \right]^{-1} \quad (\text{A12})$$

$$W_{ij}^{(e)} = w_2 \left[ \frac{\Delta \epsilon}{\hbar \omega} - 1 \right]^{\frac{1}{2}} \left[ 1 - \exp(-\hbar \omega / kT) \right]^{-1} \\ = 0 \text{ otherwise,} \quad \text{for } \Delta \epsilon > \hbar \omega \quad (\text{A13})$$

then

$$\langle [1 - (kT/2\Delta \epsilon)] W^{(i)} \rangle = \frac{1}{2} \langle W^{(i)} \rangle. \quad (\text{A14})$$

The right of (A14) can be expressed in terms of the mobility, since under our conditions

$$\langle \Delta \epsilon / W_{ii} \rangle - \langle \Delta \epsilon \tau \rangle = \langle W^{(i)} \rangle (\Delta \epsilon \tau^2) + O(W^{(i)2}), \quad (\text{A15})$$

and

$$\left[ \frac{\langle \Delta \epsilon W_{ii} \rangle}{\langle \Delta \epsilon \tau \rangle} - 1 \right] = \frac{\mu_A}{\mu} - 1, \quad (\text{A16})$$

where  $\mu_A$  is the mobility which would obtain if only the scattering by acoustic modes were present. Combination of (A11) to (A16) with (A4) and (A5) gives the results:

$$\text{Ge: } \frac{m_{44}^{(T)}}{m_{44}^{(P)}} = \frac{2}{3} \left( \frac{\mu_A}{\mu} - 1 \right) + O \left[ \left( \frac{w_2}{w_1} \right)^2 \right], \quad (\text{A17})$$

when impurity and optical mode scattering are negligible, and

$$\text{Si: } \frac{m_{11}^{(T)}}{m_{11}^{(P)}} = \frac{3}{4} \left( \frac{\mu_{A\theta}}{\mu} - 1 \right) + O \left[ \left( \frac{w_2}{w_1} \right)^2 \right], \quad (\text{A18})$$

under the same conditions, and with the additional proviso that the "g-type" scattering, which takes an electron from valley  $i$  to valley  $-i$ , have a characteristic  $\hbar \omega$  rather smaller than  $kT$ , or else be unimportant. The symbol  $\mu_{A\theta}$  represents the mobility which would result from acoustic and g-type scattering under this condition.

For germanium the intervalley scattering is probably small, and the leading term of (A17) should not be far off. If the departure of the mobility slope from the ideal value  $-\frac{2}{3}$  is attributed entirely to intervalley scattering, with the effective mass and deformation potentials assumed independent of temperature, then from figures such as  $\mu(300^\circ) = 3800$  cm<sup>2</sup>/volt sec,  $\mu(80^\circ) = 35\,000$  cm<sup>2</sup>/volt sec, we derive, for 300°K,  $(\mu_A/\mu) - 1 = 0.2$ . Although this rather arbitrary assumption may not be correct, it suggests that a value of the order of 0.15 for (A17) is not unreasonable.

For silicon the high mobility slope suggests considerable intervalley scattering, but the proper allocation of this to the  $f$  and  $g$  effects in (A3) is unknown. A value  $(\mu_A/\mu) - 1 = 0.6$  or so at 300°K would not be unreasonable, however. For this amount of intervalley scattering the higher terms of (A18) are probably appreciable, though not dominant. The leading term would then amount to 0.45; the true value would probably be less than this, but of the same order.

## APPENDIX B. IMPURITY SCATTERING

Our program will be to calculate, for each of the purer specimens of Fig. 3, the minimum value for the ratio  $\mu_A/\mu$  of acoustic to observed mobility which could be consistent with the observed piezoresistance anomaly at 10°K, if (2) holds. Then we shall discuss the difficulty of reconciling these minimum  $\mu_A$ 's with other evidence.

As was pointed out in the text, when (2) applies one gets the minimum elastoresistance for given mobility, or the maximum mobility for given elastoresistance, when impurity scattering reduces  $\mu_{\perp}$  without affecting  $\mu_{\parallel}$ . Let us therefore assume that  $\mu_{\perp} < \mu_{A\perp}$ ,  $\mu_{\parallel} = \mu_{A\parallel}$ , where the subscript  $A$  refers to acoustic scattering in a perfect crystal. From (2) and the expression for  $\mu$  given below Eq. (4) we can then express  $\mu_A/\mu$  in terms of the ratio of the  $m_{44}$  modified by impurity scattering to the ideal value  $m_{A44}$ . (We drop the superscript  $P$  for brevity and because the population effect vastly outweighs all others at the temperatures we are now considering.) The result is

$$\frac{\mu_A}{\mu} = 1 + \frac{2}{3} \left( \frac{\mu_{A\perp}}{\mu_{A\parallel}} - 1 \right) \left( 1 - \frac{m_{44}}{m_{A44}} \right). \quad (\text{B1})$$

Table III gives the values of  $\mu_A/\mu$  (10°) calculated, using (B1), from the mobilities of Fig. 8 and the values of  $m_{44}/m_{A44}$  in Fig. 3, assuming  $m_{A44}$  to be represented by the straight line. Two alternative values are assumed for  $\mu_{A\perp}/\mu_{A\parallel}$ , since values 20<sup>4</sup> and 12,<sup>13</sup> both based on

<sup>13</sup> C. Goldberg and R. E. Davis, Phys. Rev. **102**, 1254 (1956).

magnetoresistance measurements, have been reported for  $\mu_{\perp}/\mu_{\parallel}$ . We incline to favor the value 20, as we have found this to be characteristic of the purest material, less pure specimens giving values down to 11 or 12.

These values of  $\mu_A/\mu$ , which are the minimum values possible if the piezoresistance anomaly is to be attributed entirely to impurity scattering, are nearly always greater, sometimes much greater, than the ratio of the "extrapolated Hall mobility,"  $\mu_{Hex}$ , obtained by drawing a  $T^{-3}$  line through the  $80^\circ$  point for specimen 135, to the observed Hall mobility. We have to decide whether these discrepancies are larger than one could reasonably attribute to the difference between  $\mu_{Hex}/\mu_H$  and  $\mu_A/\mu$ . To begin with, we may note that both theory<sup>14,15</sup> and experiment<sup>16</sup> indicate that  $\mu_H/\mu \leq \mu_{AH}/\mu_A$  whenever the reduction of the mobility by impurity scattering is no more than a factor 4 or so. Thus to get a  $\mu_A/\mu$  higher than  $\mu_{Hex}/\mu_H$  we need  $\mu_{AH} > \mu_{Hex}$ . Departure of the geometry of the sample from ideal also does not help, since it affects  $\mu_H$  in the same way at all temperatures.

The only things remaining which could make  $\mu_{AH}$  exceed  $\mu_{Hex}$  are a value  $\mu_H < \mu_{AH}$  for specimen 135 at  $80^\circ$ , or a negative temperature exponent of  $\mu_{AH}$  greater than  $\frac{3}{2}$  between  $80^\circ$  and  $10^\circ$ . A study of Fig. 8, and of Figs. 5 and 10 of the paper of Debye and Conwell,<sup>15</sup> suggests that it is unlikely that impurity scattering or inhomogeneity reduced the mobility of specimen 135 more than a few percent below ideal at  $80^\circ\text{K}$ . It is a little more complicated to estimate how much the mobility at  $80^\circ$  may have been affected by intervalley scattering. Since the transverse branch does not contribute to the intervalley scattering,<sup>4</sup> we can probably take the characteristic temperature of the modes involved as  $\geq 300^\circ$ ; the same conclusion is suggested by the absence of any return toward a mobility exponent  $\frac{3}{2}$  as  $T$  rises to room temperature.<sup>16</sup> In such case the curves of Fig. 4, reference 2, indicate that at  $80^\circ$  intervalley scattering could have depressed  $\mu$  only about 10% below the acoustic value  $\mu_A$ , if the intervalley coupling is of the strength required to explain the observed exponent 1.66, *viz.*,  $w_2/w_1 \approx 0.3$ . A larger coupling might be possible if some other compensating cause were acting to decrease the mobility slope. However, this cause would probably also affect the slope from  $10^\circ$  to  $80^\circ$ , and so decrease  $\mu_{AH}(10^\circ)$ ; moreover, the intervalley

TABLE III. Minimum possible values of  $\mu_A/\mu$  at  $10^\circ\text{K}$  consistent with attributing piezoresistance anomalies of *n* germanium to impurity scattering, compared with a ratio of extrapolated Hall mobility  $\mu_{Hex} = 7.9 \times 10^5$  cm<sup>2</sup>/volt sec to observed  $\mu_H(10^\circ)$ .

Sample	$m_{44}/m_{444}$ at $10^\circ\text{K}$	Minimum $\mu_A/\mu$ at $10^\circ\text{K}$ for $\mu_{\perp}/\mu_{\parallel} = 20$	$= 12$	$\mu_{Hex}/\mu_H$ at $10^\circ\text{K}$
135	0.69	4.92	3.27	1.27
1008	0.64	5.55	3.64	1.84
1012	0.67	5.18	3.42	2.1
1046	0.75	4.16	2.83	3.2

scattering could not be very large without appreciably affecting the elastomagnetoresistance data of Keyes.<sup>12</sup>

As for the possibility that the acoustic mobility exponent may exceed  $\frac{3}{2}$  from  $10^\circ$  to  $80^\circ$ , such an excess could arise from temperature variation of the effective mass or deformation-potential constants. However, the temperature derivative of any such quantity should go to zero at the absolute zero, and should be significantly greater between  $80^\circ$  and  $300^\circ$  than between  $10^\circ$  and  $80^\circ$ . Therefore  $\mu_{AH}(10^\circ)$  should be quite appreciable less than the value obtained by extrapolating from  $\mu_{AH}(80^\circ)$  with the high-temperature exponent 1.66. If  $\mu_{AH}(80^\circ)$  is assumed equal to the  $\mu_H$  of specimen 135, the latter value is  $1.1 \times 10^6$  cm<sup>2</sup>/volt sec.

The gist of the preceding discussion is that it is not likely that  $\mu_{AH}(10^\circ)$  is appreciably greater than 1.0 or  $1.1 \times 10^6$  cm<sup>2</sup>/volt/sec. Even for  $\mu_{\perp}/\mu_{\parallel} = 12$  this is insufficient to account for the discrepancy in the last two columns of Table III for specimens 135 and 1008, and for  $\mu_{\perp}/\mu_{\parallel} = 20$  it fails for 1012 as well.

In the text we have made use of the conclusion that ionized impurity scattering predominated over neutral impurity scattering for all the specimens, even at  $10^\circ$ . This conclusion was reached by noting that the mobility data for the different specimens at  $10^\circ$  could be fitted fairly well by

$$1/\mu_H = 1/\mu_{AH} + an_0 + bn_{\pm}, \quad (\text{B2})$$

where  $n_0, n_{\pm}$  are the concentrations of neutral and ionized impurities, respectively, as determined from the  $N_D, N_A$  data of Table I, and  $a$  and  $b$  are fitting constants. The term  $an_0$  was of the order of 10% or less of the total for all specimens except 1043, for which it was nearly 30%. An equivalent but more direct indication of the predominance of ionized impurity scattering is provided by noting that at  $10^\circ$  the mobilities are in the inverse order of  $n_{\pm} \approx N_A$  while at  $30^\circ$  they are in the inverse order of  $N_D - N_A$ ; these two orders are different.

<sup>14</sup> H. Jones, Phys. Rev. **81**, 149 (1951); V. A. Johnson and K. Lark Horowitz, Phys. Rev. **82**, 977 (1951).

<sup>15</sup> P. P. Debye and E. Conwell, Phys. Rev. **93**, 693 (1954).

<sup>16</sup> F. J. Morin, Phys. Rev. **93**, 62 (1954).