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Piezoresistance in Heavily Doped *n*-Type Germanium†

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Piezoresistance has been measured as a function of temperature in *n*-type germanium specimens with donor concentrations between 6×10^{15} cm^{-3} and 3×10^{19} cm^{-3}. The results obtained can be explained on the basis of the accepted multivalley model, provided that statistical degeneracy is taken into account. An analysis of the degeneracy observed in the data provides strong evidence for the four-ellipsoid model of the conduction band. The data are consistent with the assumption that there is no appreciable dependence of the effective mass, deformation potential constant, and mobility anisotropy factor on the Fermi level or impurity density. No piezoresistance effect due to the (100) valleys is detected, showing that these valleys are at least 0.11 ev above the minima of the (111) valleys.

I. INTRODUCTION

MANY experiments[1–8] have demonstrated that the energy minima of the conduction band in *n*-type germanium lie on the (111) axes in **k** space. Most of the important experiments which establish this model have been performed on germanium with donor concentrations of less than 10^{16} cm^{-3}. The principal experiments which give information relevant to the band structure in highly doped germanium are measurements of magnetoresistance[8] and magnetic susceptibility.[9,10] The magnetoresistance data on specimens with donor concentrations greater than 10^{17} cm^{-3} cannot be accurately fitted by a relaxation time theory of electrical conductivity on the basis of the (111) valley model. The magnetic susceptibility measurements do not indicate any change in the band structure at high impurity concentrations. However, the susceptibility is an isotropic property, and its measurement does not establish anisotropic features of the energy bands in a unique way. It is, therefore, worthwhile to further investigate highly doped germanium with some of the experimental methods which have been helpful in elucidating the band structure of pure germanium. In this paper we shall describe measurements of the piezoresistance effect in germanium with impurity densities up to 3×10^{19} cm^{-3}.

II. THEORY

Theoretically, the piezoresistance effect in a simple multivalley semiconductor was treated by Adams[11] and Herring.[12] Herring's[12] results indicate that if the change in population due to shifts of the energy of the valleys is the major contribution to piezoresistance, the latter should vary as $1/T$. Smith[3] did not observe such a temperature dependence, but his experiments in that respect were inconclusive. A more thorough investigation of the temperature dependence of the piezoresistance in *n*-type Ge was performed by Keyes,[4] who covered a range from liquid nitrogen temperature to above room temperature, and found an inverse temperature dependence. Morin, Geballe, and Herring[5] extended the temperature range down to 4°K. They found deviations from a $1/T$ dependence at low temperatures. They believe, however, that these deviations can be explained without abandoning the accepted model for the conduction band of Ge. They suggest that their deviations from theoretical predictions are probably due to inhomogeneities in the concentration of impurities. At extremely low temperatures, impurity band conduction may also have some effect.

The model which we shall use in interpreting our piezoresistance measurements on highly doped germanium has been described by Bowers.[10] This model assumes that for high donor densities the impurity atoms have a negligible effect on the density of states at high energy levels, and that the parameters which describe the conduction band are the same as in pure germanium. The extra electrons which are added to the crystal with the donors go into the conduction band, and thus at low temperatures these electrons form a degenerate gas. This Fermi degeneracy reduces the magnitude of the piezoresistance effect as compared to the effect in pure material.

For the determination of the Fermi energy, a knowledge of the density of states is required. The density of states is proportional to the number of valleys present. According to the accepted model, the conduction band edge in Ge consists of valleys along the (111) direction. Either 4 or 8 valleys are possible in such a model, depending on whether the minima occur at the edge or inside the Brillouin zone. Because of the dependence of

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[1] Lax, Zeiger, and Dexter, Physica **20**, 818 (1954).

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[8] C. Goldberg and W. E. Howard, Phys. Rev. **110**, 1035 (1958).

[9] Crawford, Schweinler, and Stevens, Phys. Rev. **99**, 1330 (1955).

[10] R. Bowers, Phys. Rev. **108**, 683 (1957).

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[12] C. Herring, Bell System Tech. J. **34**, 237 (1955).

the piezoresistance on the number of valleys in the degenerate range, we should be able to determine which is the case.

The magnitude of the piezoresistance effect will in general depend on how the relaxation time of the carriers varies with energy. This functional dependence is not known and is probably quite complicated. In order to make calculations feasible, we assume the relaxation time to be proportional to some power of energy, $\tau \propto E^j$. Under this assumption, because of degeneracy, the classical expression for the piezoresistance constant Π_{44} in n-type Ge,

$$\Pi_{44} = -\frac{\Xi_u}{3C_{44}kT}\left(\frac{\mu_\perp - \mu_\parallel}{2\mu_\perp + \mu_\parallel}\right),$$

is modified to

$$\Pi_{44} = -\frac{\Xi_u}{3C_{44}kT}\,\frac{\mu_\perp - \mu_\parallel}{2\mu_\perp + \mu_\parallel}(j+\tfrac{1}{2})\frac{F_{j-\frac{1}{2}}(\eta)}{F_{j+\frac{1}{2}}(\eta)}, \tag{1}$$

where Ξ_u is the deformation potential constant,[13] $\mu_\perp$, $\mu_\parallel$ are the transverse and longitudinal mobilities, η is the Fermi level divided by kT and the $F_k(\eta)$ are the Fermi integrals. The exponent j, which describes the dependence of the relaxation time on energy, can be estimated from data on the temperature dependence of the resistivity,

$$\sigma(T_1)/\sigma(T_2) = (T_1/T_2)^{j+\frac{3}{2}}F_{j+\frac{1}{2}}(\eta_1)/F_{j+\frac{1}{2}}(\eta_2),$$

where T_1 and T_2 are two different temperatures, η_1 and η_2 the Fermi levels, and $\sigma(T_1)$ and $\sigma(T_2)$ the measured conductivities of a sample at those temperatures. The equation can be solved graphically for j.

Discrepancies between this very simple model and the experimental results might arise from a number of sources:

(1) The approach of the Fermi energy to higher minima in K space. Calculations by Herman[14] indicate that such minima should exist in the (000) and (100) directions.

(2) A change in the mobility anisotropy due to increased ionized impurity, electron-electron or dislocation scattering.

(3) The effective mass could vary with carrier energy within the (111) minima and could be affected by the impurities.

(4) An effect of the impurity concentration on the deformation potential, which cannot be excluded *a priori.*

As the lattice vibrations are most probably insensitive to impurity concentration, the contributions of intervalley scattering to the piezoresistance effects should not play a more important role in our case than in the nondegenerate case which has been investigated previously.

There are four minor effects which could possibly contribute to the piezoresistance,[5] namely the influence of strain on the intrinsic energy gap, the ionization energy of impurity levels, the scattering matrix elements, and the effective masses. These minor effects, should, if anything, contribute less to the total piezoresistance in highly conductive material than in high purity material. The first effect decreases with increasing concentration of carriers and the second effect entirely vanishes for the more heavily doped material.

III. EXPERIMENTAL

1. Sample Preparation

Samples of n-type Ge with impurity densities of between 6×10^{15} to 3×10^{19} cm^{-3} were used. Samples containing up to 5×10^{17} cm^{-3} were obtained from crystals grown by pulling from the melt. All samples with higher impurity density were cut out of ingots obtained by controlled cooling of a heavily doped germanium melt. Arsenic impurity was used for material up to a concentration of 8×10^{18} cm^{-3}, phosphorus impurity was used for higher impurity contents.

The geometry of the samples was similar to Smith's in "arrangement C"[3] and Keyes',[4] with the long dimension in the (110) direction. One sample with impurity content of 3.2×10^{19} cm^{-3} was prepared with the orientation of Smith's arrangement A. This sample was used to determine whether any effect on the piezoresistance due to energy minima other than those lying in the (111) direction could be detected at the carrier concentration of 3×10^{19} cm^{-3}.

The samples were lapped and etched after cutting. Electrodes, both current and voltage, were made of tin. The voltage electrodes were prepared by heating the samples in an evacuated furnace while two small pieces of tin were applied to the surface. An ultrasonic soldering iron was used for making the current electrodes. After all measurements were performed, the samples were lapped again and etched in order to make etch pit counts.

2. Hall Measurements

The number of carriers was determined from Hall voltage measurements in a way described by Bowers.[10] As the Hall effect in highly impure n-type Ge is almost independent of temperature,[10] all Hall measurements were performed at room temperature.

The Hall measurements were performed directly on the samples used for piezoresistance measurements. Moreover, in most cases, the Hall electrodes were applied at three different places to check on the homogeneity of the impurity concentration.

3. Piezoresistance and Resistivity Measurements

The method for measuring the piezoresistance is similar to that used by Smith, except that the samples

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[13] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

[14] Frank Herman, Proc. Inst. Radio Engrs. **43**, 1705 (1955).

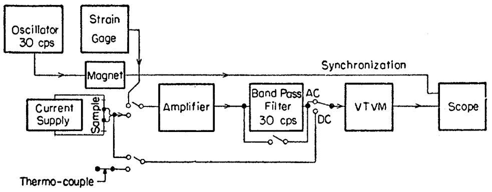

FIG. 1. The electrical block diagram of the equipment used for measurement of the piezoresistance effect.

were subjected to an alternating stress to exclude effects of temperature and other drifts on the measurements. The frequency of the strain was approximately 30 cps. Hence the measured piezoresistance constants are adiabatic. The electrical block diagram is shown in Fig. 1. The piezoresistance could be determined by measuring the cross sectional area of the sample, the ac outputs of both the strain gauge and the potential electrodes of the sample, and the dc voltage drop across the potential electrodes. The sign of the effect could be determined from the relative phases of the two ac voltages. Comparison of the wave forms of the voltages obtained from the sample and the strain gauge with the filter by-passed enabled us to determine the linearity of the piezoresistance with respect to stress.[15] For determining the resistivity, the sample current and the spacing between the potential electrodes had to be measured in addition. The latter was measured under a microscope with a calibrated sliding table.

Measurements at temperatures intermediate between 77°K and room temperature were performed in cooled methylbutane. A chromel-alumel thermocouple was employed for temperature determination.

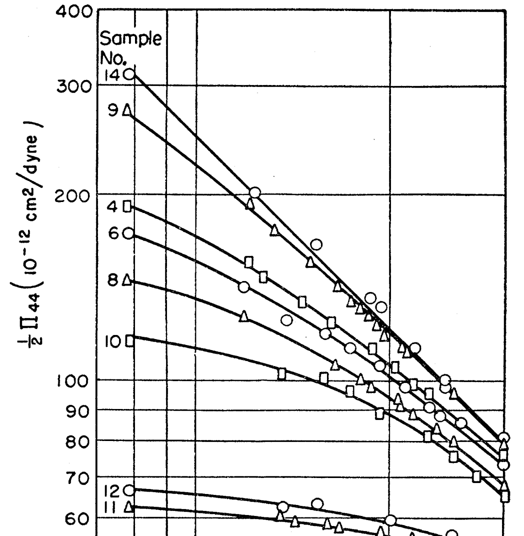

FIG. 2. The measured piezoresistance coefficient $\frac{1}{2}\Pi_{44}$ plotted against temperature for several of our samples. The solid curves here are experimental, drawn to fit the measured points.

4. Accuracy and Corrections

On some samples measurements were performed several times in order to estimate random errors. The fluctuations of the piezoresistance were less than 5%, those of resistance within a fraction of a percent.

Due to the nonuniform distribution of impurities, the appropriate impurity concentration to be used in our calculations is somewhat uncertain and is known less accurately than the electrical quantities. The value used was an average obtained from three Hall constants measured on different places on the samples. In any case, the sensitivity of the piezoresistance to the impurity content is for most measurements not very large. If, in (1), j is assumed to be zero, then

$$\Delta\Pi/\Pi = [d \ln F_{-\frac{1}{2}}(\eta)/d \ln F_{\frac{1}{2}}(\eta) - 1]\Delta n/n.$$

The factor multiplying $\Delta n/n$ is -0.15, -0.5, -0.6 for $\eta = 0, 2, 5$, respectively.

A correction is necessary to correct the measured changes in resistance $\Delta R/RX$ to the required changes in resistivity $\Delta\rho/\rho X$. This is,[3] for the samples oriented along the (110) direction, $\Delta\rho/\rho X = (\Delta R/RX) - (\frac{1}{2}S_{44} - S_{12})$; and for the sample oriented along the (100) direction, $\Delta\rho/\rho X = (\Delta R/RX) - (S_{11} - 2S_{12})$.

Another correction should be made for converting the adiabatic constants into isothermal constants. This is given by

$$\Pi_{\text{isothermal}} = \Pi_{\text{adiabatic}} + (d \ln\rho/d \ln T)(\alpha/\gamma C),$$

where α is the thermal expansion coefficient, γ the density, and C the specific heat. All the constants necessary for those corrections are well known,[16] and $d \ln\rho/d \ln T$ can be obtained from our resistivity measurements.

TABLE I. Some specifications of the samples used. n is the average carrier concentration as obtained from three Hall measurements; Δn is the deviation from the average.

Sample No.	n (cm^{-3})	Δn%	Etch pit count (cm^{-2})
1	2.7×10^{18}	8	0.8×10^{5}
2	5.1×10^{18}	27	3×10^{5}
3	2.5×10^{18}	14	1.6×10^{5}
4	2.2×10^{18}	7	2.2×10^{5}
5	3.0×10^{18}	3	1.8×10^{5}
6	3.1×10^{18}	10	1.2×10^{5}
7	4.1×10^{18}	22	1.5×10^{5}
8	3.8×10^{18}	6	1.1×10^{5}
9	5.0×10^{17}		0.2×10^{5}
10	6.8×10^{18}	16	2.9×10^{5}
11	2.0×10^{19}	19	1.2×10^{5}
12	1.9×10^{19}	20	0.7×10^{5}
13	1.7×10^{19}	25	0.7×10^{5}
14	6×10^{15}		0.8×10^{5}
15	3.0×10^{19}		
16	3.2×10^{19}	12	

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[15] A description of the method will be published elsewhere.

[16] E. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

IV. RESULTS

In Table I, all of the samples are listed with information about their impurity concentration and etch pit counts. The concentration given is an average obtained from the three Hall constants. Δn is the spread of those measurements around the average. The etch pit counts are considered as a rough approximate measure of the dislocation density. The long direction of samples 1–15 is along (110) and that of sample No. 16 is along (100). Numbers not recorded in the table were not measured. The direct results of our piezoresistance measurements are plotted for several samples in Fig. 2. The results are uncorrected in the sense of the previous paragraph. The dimensional correction is -1×10^{-2} cm^2 dyne^{-1}, hence constitutes at the most 2% of the measured piezoresistance and can be neglected. The isothermal correction is even smaller, as for the largest $d\ \ln\rho/d\ \ln T$ the correction is 1×10^{-12} cm^2 dyne^{-1}. This is for sample 14 (concentration 6×10^{15} cm^{-3}). For all other samples $d\ \ln\rho/d\ \ln T$ is much smaller at all temperatures, and this correction is therefore completely negligible for all degenerate samples.

Figure 3 gives the results for all samples oriented along the (110) direction. The piezoresistance is plotted here against the impurity content with the temperature as a parameter. The points are obtained from experimental curves of the type illustrated on Fig. 2. The solid lines correspond to the theoretical value, assuming four valleys and $j=0$, using for the factor $\Xi_u(\mu_\perp-\mu_{\parallel})/(2\mu_\perp+\mu_{\parallel})$ appearing in Eq. (1), the value obtained from experiments on the pure material.

The assumption $j=0$ is made on the basis of resistivity data. This is a good approximation only for samples with impurity concentrations around 5×10^{18} cm^{-3}. At low concentrations, j has a value larger than zero, but its influence on the piezoresistance is small due to the low degree of degeneracy. At high impurity concentration, j has a small value and a larger influence on the piezoresistance. For a sample of 3×10^{19} impurities cm^{-3}, the value of j obtained from conductivity measurements at 77°K and 300°K is -0.5. However, the dependence of the conductivity on temperature indicates that at this concentration the relationship $\tau\propto E^j$ is no longer a good assumption. Indeed, the observed dependence is far from monotonic, but rather reveals maxima and minima. One would obtain therefore values for j ranging from positive to negative numbers from conductivity data gathered at different temperatures. The theoretical curves in Fig. 3 are drawn with $j=0$ for all values of concentration for the sake of simplicity. In view of the preceding remarks, however, no conclusions which involve the energy dependence of the mobility are drawn for samples with 3×10^{19} impurities cm^{-3}.

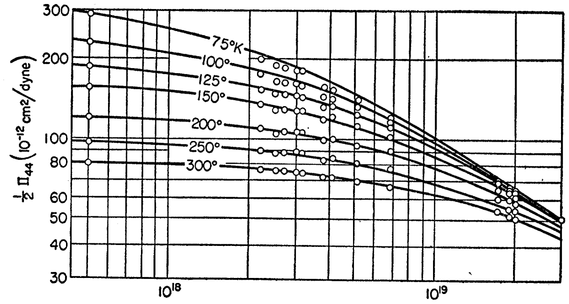

FIG. 3. The piezoresistance coefficient $\frac{1}{2}\Pi_{44}$ plotted against impurity concentration, with temperature as a parameter. The experimental points are obtained from graphs of Fig. 2. The solid lines are a plot of Eq. (1), assuming mobilities independent of energy ($j=0$). The value of $\Xi_u(\mu_\perp-\mu_{\parallel})/(2\mu_\perp+\mu_{\parallel})$ is chosen so as to make the calculated and observed piezoresistance coincide for nondegenerate material.

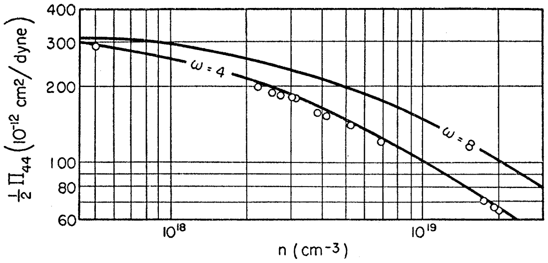

FIG. 4. Comparison of theoretical piezoresistance curves for models with 4 and 8 valleys with experimental data. $\frac{1}{2}\Pi_{44}$ is plotted against impurity concentration. The graph corresponds to a temperature of 75°K.

The data obtained seem to indicate that the model adopted for the edge of the conduction band of Ge on the basis of experiments performed on pure *n*-type Ge (cyclotron resonance,[1,2] elastoresistance,[3–5] and others[6–8]) holds at least up to energies of approximately 0.05 ev, corresponding to concentrations of carriers of 2×10^{19} cm^{-3}. Furthermore the presence of the impurities does not seem to affect this model. The results also indicate clearly that the number of valleys is 4. The fit to the curves of Π_{44} as a function of concentration and temperature, calculated on that assumption are remarkably good, whereas an assumption of 8 valleys would not agree with our experiments. The discrepancy can be seen, if one imagines, on Fig. 3, the experimental points shifted to the left with respect to the theoretical curves by an amount corresponding to a factor of two on the logarithmic scale of carrier concentration. A comparison of experimental data with 4- and 8-valley models at 75°K is shown in Fig. 4. The result based on the use of 4 valleys is in agreement with the interpretations of Crawford, Schweinler, and Stevens[9] and Bowers[10] of their respective experiments on magnetic susceptibility on highly impure *n*-type Ge.

The mobility anisotropy factor in Eq. (1), $K=(\mu_\perp-\mu_{\parallel})/(2\mu_\perp+\mu_{\parallel})$, does not seem to be affected appreciably by the impurity content. This, however, does not mean that the ratio $\beta=\mu_\perp/\mu_{\parallel}$ does not change appreciably, as the anisotropy factor is very insensitive to changes in this ratio: $\Delta K/K_0\cong1.5\beta_0^{-1}(\Delta\beta/\beta_0)$. As $\beta_0\cong20$ it is evident that $\mu_\perp/\mu_{\parallel}$ can change substantially without affecting appreciably the piezoresistance. The accuracy of our measurements of piezoresistance being $\pm 3\%$, the influence of mobility anisotropy would be undetected, unless β changed by $\sim 50\%$. In our samples ionized impurity scattering, which is most effective at low temperatures, is expected to predominate. Such scattering might be expected to decrease the mobility anisotropy and hence the piezoresistance. It will be noted in Fig. 3 that in the region where $j=0$ is a good assumption, the observed piezoresistance at low temperatures falls below the theoretical curves. Should the scattering be responsible for this deviation, it would mean a change in β by roughly a factor of 2 from pure material to a concentration of $4\text{-}5\times 10^{18}$ cm^{-3} at liquid nitrogen temperature. In accordance with Morin, Geballe, and Herring's work,[5] there is another possible explanation for the decreased piezoresistance at low temperatures. The latter believe that this phenomenon is explicable in terms of microscopic inhomogeneities. Our observations provide some evidence for this belief because in our experiments deviation was only observed in the arsenic-doped specimens and not in the phosphorus-doped specimens, and we believe that the phosphorus-doped samples are more homogeneous than those doped with arsenic.

A possible effect to which our measurement should be sensitive is the change of effective mass with varying energy of the carriers. If $m^* = m_0 + \Delta m(E)$, where m_0 is the effective mass at the bottom of the conduction band and Δm can be expanded to first order, $\Delta m = \mu E$, then $\Delta\Pi/\Pi = \frac{3}{2}\eta^{-1}\{d/d\eta[F_{\frac{3}{2}}(\eta)/F_{\frac{1}{2}}'(\eta)]\}(\mu E_F/m_0)$.

For samples of carrier concentrations of 2×10^{19} cm^{-3}, the coefficient of $\mu E_F/m_0$ is 0.7 at 75° and 1.4 at 300°: The deviation of the piezoresistance from a constant mass model should therefore be of the same order as the deviation of the effective masses at the Fermi energy from those at the conduction band edge. According to our data there is no evidence of a change in effective masses up to energies of 0.05 ev above the conduction band edge. This result is again in agreement with Bowers' work.[10]

Changes in the deformation potential should be easily detectable by measuring the piezoresistance, as the two are proportional. Our results then indicate that there is no appreciable effect of the impurity content on the deformation potential, at least up to 2×10^{19} impurities per cm^3.

Another effect which should be easily detected in the piezoresistivity is the approach of the Fermi level to some other minimum in K space. Presumably such a minimum would be located at (000) or in the (100) directions. The first case should not add any additional independent constants to the piezoresistance tensor, but merely decrease the large piezoresistance constant. Because of the uncertainty about j at high impurity concentrations not much can be concluded about the first case.

The measurements on sample 16 should be sensitive to the second situation [valleys in the (100) direction]. In order to investigate this situation, sample 16 was oriented very carefully within a fraction of a degree, in order to eliminate admixtures of piezoresistance effects due to (111) valleys from the measurements. The magnitude of the piezoresistance observed at 300°K was approximately 1×10^{-12} cm^2 dyne^{-1} which is only about 2% of the large coefficient. This probably should be attributed to the minor effects. In any case we can evaluate a lower limit for the energy separation between the (100) and (111) minima. Such an energy can be calculated from statistical mechanics if we know the effective mass parameters for the valleys and the electron populations. For the (100) effective mass parameters, we use, as a reasonable guess, those which characterize the (100) valleys in silicon. From the magnitude of elastoresistance in sample 16, we estimate that no more than 5% of the electrons are in the (100) valleys at 300°K in that sample. We obtain thereby an energy difference of 0.11 ev. Since 5% is a liberal estimate, we conclude that the energy difference between the (100) and (111) valleys must be at least 0.11 ev.

V. SUMMARY

The dependence of the piezoresistance effects on temperature and concentration for highly impure n-type Ge indicates that the lowest 0.05 ev of the energy band is well represented by the accepted model. The presence of 2×10^{19} ionized donors cm^{-3} does not effect the conduction band appreciably.

The number of valleys present along (111) is four; hence the edge of the conduction band must occur at the edge of the Brillouin zone.

If a reduction in the mobility anisotropy exists, it is not extremely large. The ratio $\mu_\perp/\mu_{\parallel}$ is not reduced to a lower value than 10, its value for pure material being 20.

There is no evidence for a change of curvature of the conduction band up to 0.05 ev above the edge of the valley. It is improbable that the effective mass and mobility anisotropy should both change in such a way that the piezoresistance should remain unaffected.

According to our data the (100) and (111) minima are more than 0.11 ev apart. The experiment was inconclusive with respect to the location of the (000) minimum of the conduction band.

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