

High-Stress Piezoresistance in Degenerate Arsenic-Doped Germanium*

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The resistivity of germanium containing between $N=4 \times 10^{17}$ and 10^{19} arsenic atoms per cc was measured at 1.2°K under uniaxial compressions of up to 10^{10} dyn cm⁻². The piezoresistance fails to saturate near the stress at which one expects essentially all electrons to have been transferred to a single conduction band valley ([111] compression) or to two valleys ([110] compression). Saturation is approached at much higher stresses. The resistivity was measured for current flowing parallel and perpendicular to the stress direction. For $N > 10^{18}$ cm⁻³, the mobility anisotropy was found to be $\mu_{\perp}/\mu_{\parallel} = 4 \pm 0.4$, 5 ± 0.6 , and 6 ± 0.5 for the 4-, 2-, and 1-valley cases, respectively. The mobility ratio $\mu_{\parallel}(\text{Sb})/\mu_{\parallel}(\text{As})$ increases from about 1.5 to 1.9 as the electrons are transferred from 4 valleys to 1 valley. Evidence for the presence of tail states in As-doped germanium and the significance of the large central impurity cell potential of As donors for the interpretation of the piezoresistance are discussed.

I. INTRODUCTION

BY applying large shear stresses it is possible to change a multivalley semiconductor or one with degenerate bands into a simple semiconductor in which the charge carriers are confined to one region in k space which has a simple ellipsoidal shape. This method has been used recently for the determination of deformation potentials,^{1,2} and for studying the effect of stress on the impurity wave functions in n -Ge,³ and p -Ge.⁴ In degenerate n -Ge this method allows the direct measurement of the mobility anisotropy of the carriers in one conduction band valley.^{5,6} Having this parameter one might try to treat the semiconductor like a metal under residual resistance conditions and obtain information about the mobility and its dependence on energy and impurity concentration which can be compared with theory.⁶ In the case of Sb-doped degenerate germanium fairly good agreement was found between the experimental results of two different laboratories.^{5,6} However, rather large discrepancies were found⁶ between these results and theoretical calculations of ionized impurity scattering based on an individual scattering model.⁷

The experimental situation is much less certain in the case of As-doped degenerate germanium. The mobility anisotropy of a single valley has not been measured directly and very different values are obtained from this

quantity by different authors depending on the model used for interpreting the experimental results.^{5,8}

The case of As-doped Ge is more complicated than that of Sb-doped Ge because of the much larger central cell potential, which gives rise to the valley-orbit splitting of the isolated donor impurity levels of the As donors.¹ This important difference between Sb and As donors in germanium is apparent in many experiments. The large magnitude of intervalley scattering⁹ and of the impurity-assisted interband tunneling^{10,11} and the presence of a negative magnetoresistance effect¹² at high doping levels in As-doped Ge are indications of the effect of the large central cell potential of the As donors.

In order to evaluate the validity of the different models used for the description of As-doped degenerate germanium, we have extended the piezoresistance measurements to higher stress values and higher As concentrations and obtained the mobility anisotropy directly by measuring the resistivity parallel and perpendicular to the valley axis. The range of As concentrations extends from 4×10^{17} to 10^{19} cm⁻³. Uniaxial compressional stresses of up to 10^{10} dyn/cm² along the [111] and the [110] axes were used. The piezoresistance measurements were carried out at 1.2°K.

II. EXPERIMENTAL DETAILS AND RESULTS

The stress apparatus, the cryostat, and the sample preparation are the same as those used for Sb-doped

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¹ H. Fritzsche, Phys. Rev. **115**, 336 (1959).

² S. H. Koenig and J. J. Hall, Phys. Rev. Letters **5**, 550 (1960); J. J. Hall, Phys. Rev. **128**, 68 (1962).

³ H. Fritzsche, Phys. Rev. **125**, 1552 (1962); **125**, 1560 (1962).

⁴ F. Pollak, Phys. Rev. **138**, 618 (1965).

⁵ S. H. Koenig, *Report on the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society of London, 1962), p. 5; M. J. Katz, Helv. Phys. Acta **35**, 511 (1962).

⁶ M. Cuevas and H. Fritzsche, Phys. Rev. **137**, A1847 (1965).

⁷ P. Csavinszky, Phys. Rev. **131**, 2033 (1963).

⁸ H. Fritzsche and M. Cuevas, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1962), p. 29.

⁹ W. P. Mason and T. B. Bateman, Phys. Rev. **134**, A1387 (1964); P. J. Price and R. L. Hartman, J. Phys. Chem. Solids **25**, 567 (1964).

¹⁰ R. N. Hall, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 193.

¹¹ Y. Furukawa, J. Phys. Soc. Japan **15**, 1903 (1960).

¹² W. Sasaki and Y. Kanai, J. Phys. Soc. Japan **11**, 894 (1956); Y. Furukawa, J. Phys. Soc. Japan **17**, 630 (1962); **18**, 1374 (1963).

germanium described earlier.⁶ The samples are listed in Table I. The arsenic concentration N was obtained from Hall measurements at 300 or 78°K using $R = (eN)^{-1}$ and a field of 7000 G. The Hall coefficients may differ by a few percent at these two temperatures; the R value of smallest magnitude was then used for the calculation of N . The uncertainty in R is about $\pm 3\%$. The letters C , F , and G in the sample notation symbolize the same stress and current orientations as explained in Table II of Ref. 6. The letter D is used for the perpendicular arrangement: uniaxial compression X along $[110]$ and current I along $[1\bar{1}0]$.

In the upper part of Fig. 1 the resistivities ρ measured at 300, 78, and 1.2°K are plotted against the As concentration. The deviations of the individual data points from the smooth curves indicate the combined uncertainty in the homogeneity and composition of the samples and in the determination of ρ and N . In the lower part of Fig. 1 the corresponding data for Sb-doped germanium are plotted for comparison. The ρ versus N curves at 300°K agree well with those reported by other workers.^{13,14} The concentration dependence of ρ is stronger at 78 and 1.2°K than at 300°K. It is interesting to note that the resistivities at 1.2°K are lower than those at 78°K by a factor which is nearly independent of N in this range. This negative temperature

TABLE I. Sample characteristics.

Sample	N 10^{18} cm^{-3}	E_{F0}^a (eV)	$E_{F_{\text{sat}}}^b$	μ_0^a at 1.3°K ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$)	μ_{sat}^b at 1.3°K ($\text{cm}^2 \text{sec}^{-1} \text{V}^{-1}$)
As-F-1	0.330	0.0031	0.0079	36.6	44.8
As-F-2	0.405	0.0036	0.0090	175	64.5
As-F-3	0.934	0.0062	0.0156	816	131
As-F-4	1.43	0.0083	0.0210	761	125
As-F-5	1.66	0.0091	0.0233	732	126
As-F-6	3.39	0.0147	0.0378	659	118
As-F-7	4.59	0.0181	0.0460	612	118
As-C-1					
As-C-2					
As-C-3	0.85	0.0058	0.0094	785	427
As-C-4	1.47	0.0085	0.0134	764	429
As-C-5	2.82	0.0131	0.0210	738	399
As-C-6	4.04	0.0165	0.0265	677	364
As-C-7	7.26	0.0245	0.0395	578	303
As-C-8	10.5	0.0320	0.0505	529	281
As-D-1	1.47	0.0084	0.0135	760	850
As-D-2	1.78	0.0096	0.0151	778	860
As-D-3	2.27	0.0112	0.0180	764	840
As-D-4	2.44	0.0117	0.0189	747	850
As-D-5	4.37	0.0175	0.0280	649	750
As-D-6	5.03	0.0192	0.0307	655	770
As-D-7	7.27	0.0245	0.0395	569	680
As-D-8	10.5	0.032	0.050	523	630
As-G-1	2.10	0.0107	0.0273	724	770
As-G-2	2.20	0.0110	0.0280	714	760
As-G-3	2.64	0.0125	0.0320	757	810
As-G-4	3.01	0.0136	0.0350	728	780
As-G-5	3.78	0.0159	0.0405	670	710
As-G-6	4.50	0.0180	0.0455	657	710
As-G-7	5.88	0.0214	0.0550	599	610

^a The subscript 0 stands for zero stress.

^b The subscript "sat" stands for saturation.

¹³ Y. Furukawa, J. Phys. Soc. Japan **15**, 730 (1960); W. G. Spitzer, F. A. Trumbore, and R. A. Logan, J. Appl. Phys. **32**, 1822 (1961).

¹⁴ T. Seidel, *Metallurgy of Elemental and Compound Semiconductors*, edited by R. O. Grubel (Interscience Publishers, Inc., New York, 1961), p. 453.

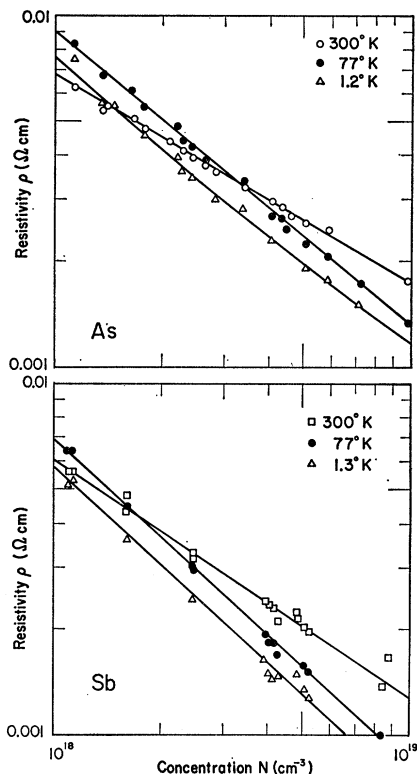


FIG. 1. Resistivity as a function of donor concentration for As- and Sb-doped germanium at 1.2, 77, and 300°K.

coefficient of the mobility has been noted before and several models have been proposed for its explanation.^{5,15}

Figures 2 and 3 show the relative change of the resistivity $(\rho_x - \rho_0)/\rho_x$ as a function of compressional stress X at 1.2°K for the two longitudinal cases F and C , respectively. The arrows indicate the stress value at which saturation of $\Delta\rho/\rho$ is expected to occur according to the simple degenerate model, that is the stress above which all electrons are transferred from the higher valleys to the lower valley or valleys in the absence of band tailing.

Sample As-F-1 shows a behavior which is similar to that of As-doped germanium in the intermediate concentration range reported earlier,³ an initial increase followed by a decrease of ρ as X increases. At that time the decreasing and negative piezoresistance at higher stresses was qualitatively explained as caused by an increase of the effective radius of the As donor wave function as the donor binding energy is decreased by the stress.³ Sample As-F-2 appears to be a borderline case. For $N > 9 \times 10^{17} \text{ cm}^{-3}$ the saturation of $\Delta\rho/\rho$ expected for degenerate samples seems to set in. However, in contrast to Sb-doped Ge⁶ the piezoresistance goes through a maximum before it slowly saturates at large stress values. This maximum is even more strongly pronounced in the C orientation shown in Fig. 3. Here

¹⁵ T. N. Morgan, Bull. Am. Phys. Soc. **8**, 224 (1963).

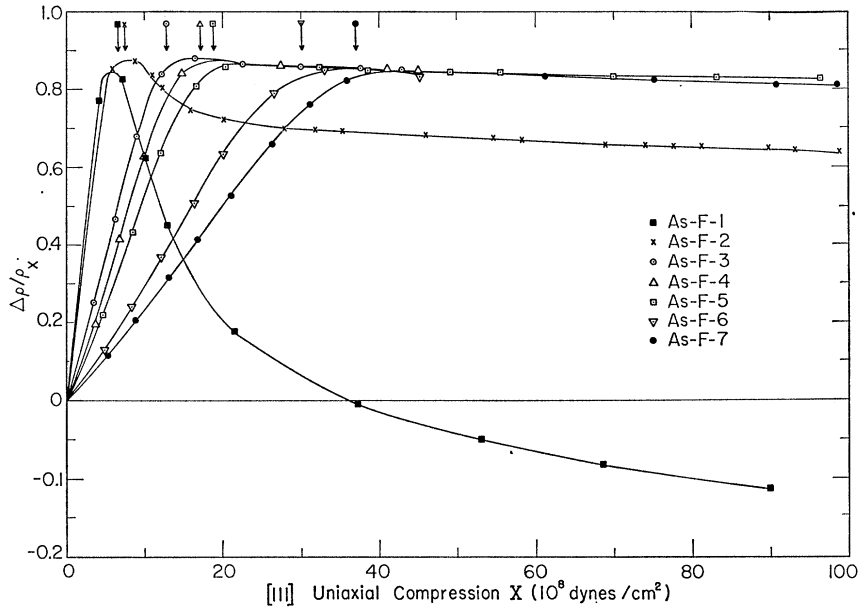


FIG. 2. Longitudinal piezoresistance as a function of [111] compressional stress (arrangement \bar{F}) at 1.2°K for As-doped germanium. The arrows indicate for each sample the stress at which saturation is expected for undistorted parabolic bands.

again samples As-C-1 and As-C-2 represent borderline cases between the impurity conduction phenomena at lower N and the degenerate region. These maxima in the $\Delta\rho/\rho$ curves occur at stresses which lie $3-5 \times 10^8$ dyn/cm² and $4-6 \times 10^8$ dyn/cm² higher than the theoretical saturation stresses X_s for orientation \bar{F} and \bar{C} , respectively. The magnitude of this shift is similar to that between X_s and the onset of saturation in Sb-doped Ge.⁶

The results of the transverse measurements for orientations $D(X[110])$ and $I[\bar{1}\bar{1}0])$ and $G(X[111])$ and $I[\bar{1}\bar{1}0])$ are shown in Figs. 4 and 5, respectively. These measurements have to be interpreted with great caution because of the stress inhomogeneities which occur in the transverse stress arrangement as explained earlier.⁶ It

was argued at that time that although the low-stress results are affected by additional frictional stresses, the saturation values of the transverse piezoresistance should be correct. As shown in Figs. 4 and 5 most of the $\Delta\rho/\rho$ curves fail to saturate in the available stress range. This introduces some uncertainty in the quantitative analysis of the results.

The transverse piezoresistance curves of Fig. 5 and those of Sb-doped germanium of the same orientation \bar{G} (see Fig. 4 of Ref. 6) are very similar up to the theoretical saturation stress X_s indicated by vertical arrows for each sample. Whereas the $\Delta\rho/\rho$ curves of the Sb-doped samples reach a saturation value of the order of 0.075 beyond X_s the $\Delta\rho/\rho$ curves of the As-doped samples go through a maximum and decrease to negative values at

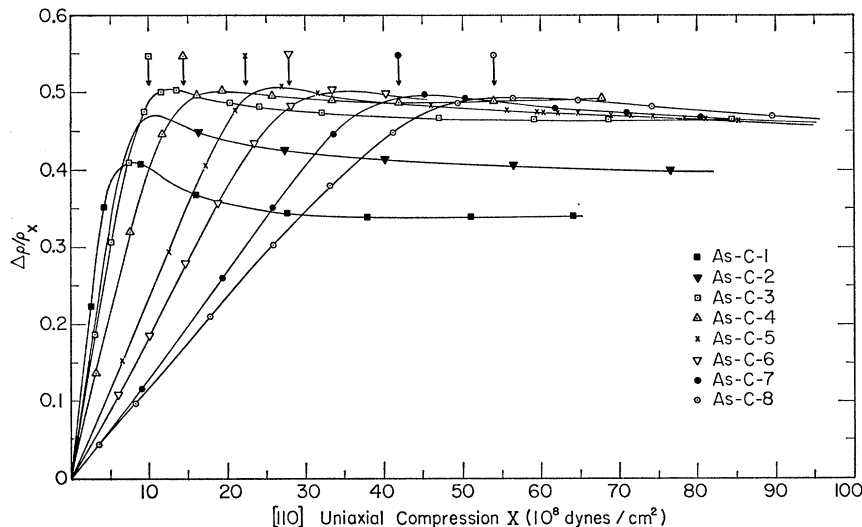
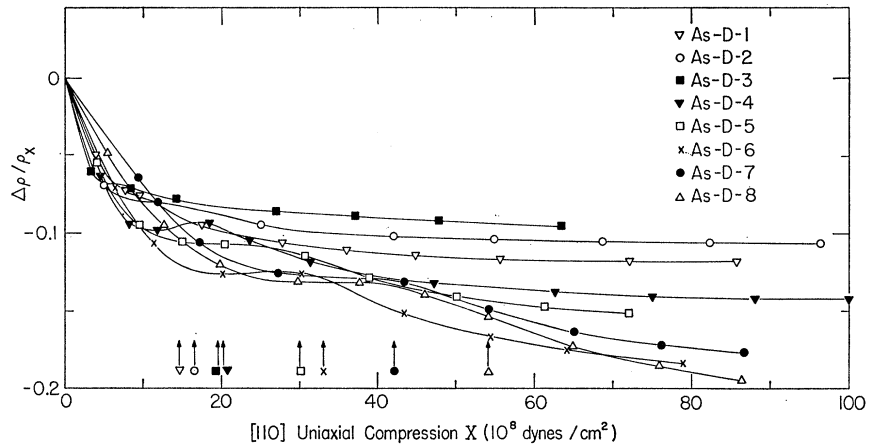


FIG. 3. Same as Fig. 2 for [110] compressional stress (arrangement \bar{C}).

FIG. 4. Transverse piezoresistance as a function of $[110]$ compressional stress with current along $[110]$ at 1.2°K for As-doped germanium (arrangement D). The arrows indicate the saturation stress for undistorted parabolic bands.



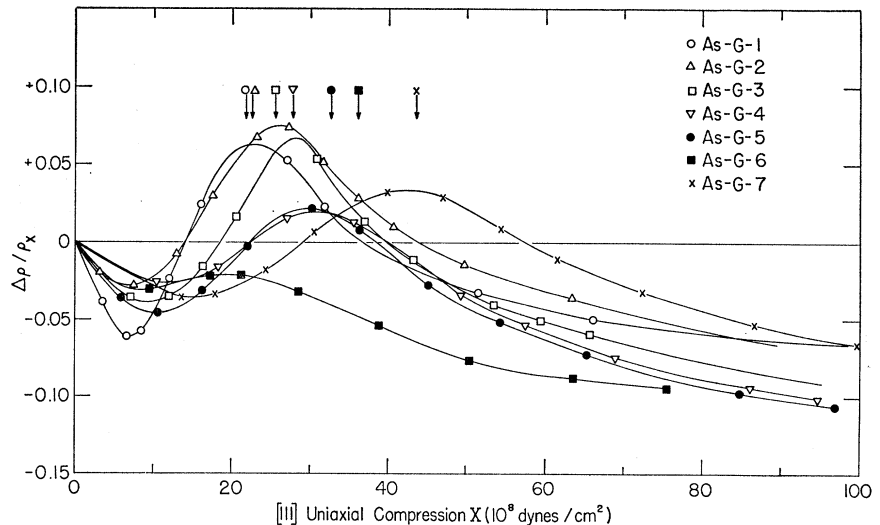
large stresses. This decrease is considerably larger than that observed in orientation F : about 0.1 compared to about 0.04 for case F (see Fig. 2). Also, the curves in Fig. 4 show a tendency to saturate followed by a subsequent decrease of $\Delta\rho/\rho$. The fact that the change of $\Delta\rho/\rho$ beyond X_s is larger for orientations G and D than for F and C , respectively, is consistent with Koenig's explanation⁵ for this effect: If localized electron states remain associated with the valleys moving upwards with stress, then these immobile electrons transfer into the lowered valley or valleys at stresses larger than X_s . An electron originating from such levels will contribute a larger increase in conductivity for current orientations in the high mobility directions (cases G and D) than for the low mobility orientation (cases F and C). Furthermore, more immobile electrons become available beyond X_s when 3 valleys are moved up by stress (cases F and G) than when 2 valleys are raised (cases C and D). The absence of the decrease of $\Delta\rho/\rho$ beyond the onset of saturation in Sb-doped Ge would then imply that the

number of such localized states is negligible for that material.

It is instructive to point out the differences and similarities of the two donor elements Sb and As in germanium with regard to their effects on the mobilities and the piezoresistance effects. Figure 6 shows the low-stress piezoresistance coefficient Π_{44} as a function of Sb and As concentration. Our values are in fair agreement with those of Katz and Koenig.⁵ They are significantly larger, however, than the extrapolation into the high concentration range of the results of Nakamura and Sasaki.¹⁶

Figure 7 shows for Sb⁶ and As donors the concentration dependence of the zero stress mobility (4-valley case) and of the mobility components parallel and perpendicular to the respective stress directions for the 2- and 1-valley cases. The results were obtained at 1.2°K from the resistivities in the very high stress limit under the assumption that the carrier concentration is not changed by the stress.

FIG. 5. Same as Fig. 4 for $[111]$ compressional stress (arrangement G).



¹⁶ M. Nakamura and W. Sasaki, J. Phys. Soc. Japan **19**, 236 (1964).

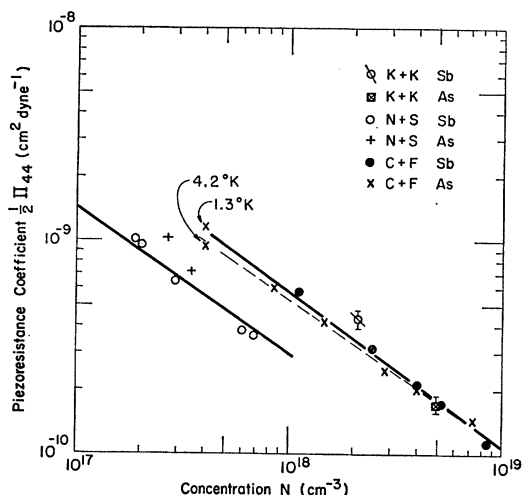


FIG. 6. Low stress piezoresistance coefficient $\frac{1}{2}\Pi_{44}$ as a function of donor concentration. The dashed line indicates the theoretically expected slope $\Pi_{44} \propto N^{-2/3}$. The letters behind the data symbols stand for the investigators: $K+K$ =Koenig and Katz (Ref. 5 of text), $N+S$ =Nakamura and Sasaki (Ref. 16 of text), $C+F$ =present authors (see also Ref. 6 of text).

The Hall coefficients obtained at 300 or 77°K were used to determine N and the mobilities in this figure because the Hall coefficients could not be measured at large stresses with the present apparatus. Since the Hall coefficient becomes temperature-dependent for $N < 8 \times 10^{17} \text{ cm}^{-3}$, the plotted curves do not represent the true Hall mobilities and the abscissa is not the Hall concentration in this lower concentration range. The curves shown in Fig. 7, therefore, fall off much more rapidly with decreasing N than those of Furukawa.¹² The vertical arrows indicate the critical concentrations N_c at which the thermal activation energy ϵ_2 of impurity conduction vanishes.^{3,6} The different values of N_c and the different behavior of the mobility curves below $N = 8 \times 10^{17} \text{ cm}^{-3}$ for the 4 and 1 valley cases and for Sb and As doping may be explained qualitatively as being due to the different effects of the valley-orbit splitting energies on the donor wave functions.

At the higher concentrations $N > 10^{18} \text{ cm}^{-3}$ we observe the following:

1. The concentration dependence of the mobility components is different for Sb and As doping. At zero stress and 1.2°K, for example, one finds for Sb, $\mu(4) \propto N^{-0.19}$; and for As, $\mu(4) \propto N^{-0.22}$. This concentration dependence is significantly less than the $N^{-0.5}$ dependence obtained at 4.2°K from the free carrier absorption at a wavelength of 2.4μ .^{17,18}

¹⁷ T. I. Pancove, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (John Wiley & Sons, Inc., New York, to be published), Vol. 9.

¹⁸ At 300°K the concentration dependence of the Hall mobility is $N^{-0.4}$ for As-doped germanium. Hence the discrepancy between electrical and optical measurements is less at the higher temperatures.

2. The mobilities begin to decrease with increasing N and show a simple power law dependence on N at a lower concentration for As than for Sb. This is surprising since one would expect the onset of "metallic" conduction to occur at higher concentrations for As than for Sb for the same reason³ which causes the difference in N_c .

3. The mobilities $\mu(4)$ of unstressed Ge doped with As are lower by a factor of about 1.4 than those of Ge doped with Sb. The ratio of $\mu_{11}(1)$ of Sb to $\mu_{11}(1)$ of As (orientation F) is as large as 1.9 at large concentrations. For the transverse direction (orientation G) the ratio $\mu_{11}(1)$ of Sb to $\mu_{11}(1)$ of As is about 1.3.

4. The low stress piezoresistance coefficient Π_{44} is the same for Sb and As doping within the experimental accuracy (see Fig. 6). For $N > 10^{18} \text{ cm}^{-3}$, the concentration dependence is close to $\Pi_{44} \propto N^{-2/3}$ as expected from theory.

5. In contrast to the case of Sb doping the piezoresistance of As-doped Ge decreases beyond the saturation stress X_s and approaches a constant value only at higher stresses. This decrease is larger for the high mobility orientations G and D than for the low mobility orientations F and C .

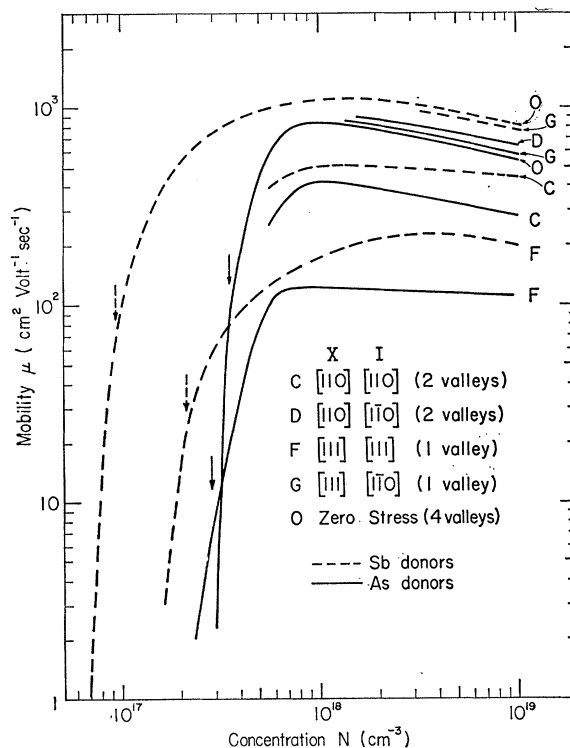


FIG. 7. Mobility components along the current direction in arrangements $C, D, F,$ and G at 1.2°K are plotted versus concentration. These components were determined from the saturation values of the piezoresistance in these arrangements and the Hall coefficient as measured in the exhaustion region. The arrows indicate the critical concentrations N_c at which the activation energy for impurity conduction vanishes. The dashed and full lines represent Sb- and As-doped germanium, respectively.

III. DISCUSSION

Previous analyses^{5,6,8} of the transport properties of degenerate germanium were based on the simple degenerate model with the following assumptions.

1. The mobility components, μ_{11} and μ_{\perp} , parallel and perpendicular, respectively, to the valley axis, depend explicitly on concentration N and Fermi energy E_F , e.g.,

$$\mu \propto N^r E_F^s, \quad (1)$$

where the values of r and s may depend on the number of lower valleys and hence on stress because of screening effects and a changing contribution of intervalley and electron-electron scattering.

2. The bands are parabolic so that the Fermi energy E_F increases as

$$E_F \propto N^{2/3}. \quad (2)$$

With this the total N dependence of μ becomes

$$\mu \propto N^{r+2s/3}. \quad (3)$$

3. The total carrier concentration is independent of stress in the degenerate concentration region.

Assumption (1) yields for the low stress piezoresistance coefficient Π_{44}

$$\Pi_{44} = -\frac{1}{3} \frac{K-1}{2K+1} \left(\frac{3}{2} + s\right) \frac{E_2 S_{44}}{E_F}, \quad (4)$$

where the mobility anisotropy $K = \mu_{\perp}/\mu_{11}$ and the value of s refer to the 4 valley case. E_2 is the shear deformation potential¹ and S_{44} the elastic compliance constant.

If the values of K , r , and s were independent of the distribution of the electrons over the valleys and hence of stress, then it would be a simple matter to determine these values from the low-stress and high-stress piezoresistance and from the N dependence of μ . This, however, is not the case as one can see immediately (Fig. 7) from the fact that $\mu(1)$, $\mu(2)$, and $\mu(4)$ depend differently on N . In this case further assumptions are required in order to analyze the data with the simple degenerate model.

Koenig and Katz⁵ assume for the interpretation of their results that $r = -1.0$. With this one can obtain the value $s(4)$ for the 4 valley case from the N -dependence of $\mu(4)$ using Eq. (3), and subsequently one can obtain the value $K(4)$ from the low stress piezoresistance using Eq. (4). Katz also determined $K(4)$ from the stress dependence of the Hall coefficient at 77°K. He found that both methods yield a value of $K(4)$ between 2.1 and about 3.4 for an As concentration of $N = 5 \times 10^{18} \text{ cm}^{-3}$.

The assumption $r = -1.0$ appears to be the weakest link in the chain of this analysis. For germanium in this concentration range Csavinszky's theory^{7,6} of scattering at independent donor ions predicts for the 4 valley case $r(4) = -0.71$ because of the concentration-dependent screening effects. A failure of the individual scattering

hypothesis is expected to result in even smaller magnitudes of r .

If we analyze our values of Π_{44} with Koenig's method but assume $r(4) = -0.72$ according to the results on Sb-doped Ge,⁶ and if we use our value $r(4) + 2s(4)/3 = -0.22$, then we obtain for As-doped germanium $s(4) = 0.75$ and $K(4) = 4.0 \pm 0.4$.

The mobility anisotropy $K(4)$ has also been determined from magnetoresistance measurements,¹⁹ particularly from the saturation of the longitudinal magnetoresistance.²⁰ Different authors^{19,20} quote for As-doped germanium values increasing from $K=7$ to $K=9$ between $N=10^{18}$ and 10^{19} cm^{-3} and from $K=3.5$ to $K \approx 6$ between $N=10^{18}$ and $6.2 \times 10^{18} \text{ cm}^{-3}$. These data were taken near 77°K but at these high concentrations K should be nearly temperature-independent. Tsidilkovski *et al.*²⁰ quote an error of 10% for their magnetoresistance values. This gives rise to a 15–20% error in their determination of K . Furthermore, the value $K \approx 6$ at $N = 6.2 \times 10^{18} \text{ cm}^{-3}$ was obtained from the low field magnetoresistance and is therefore even less certain. Our value $K(4) = 4.0 \pm 0.4$ lies within these limits of uncertainty. The rather large K values quoted by Fistul *et al.*²⁰ were obtained from the low field magnetoresistance. They are again subject to the validity of the assumptions made in interpreting the low field results.

The values for $K(1)$ and $K(2)$ can in principle be obtained from the high stress longitudinal and transverse piezoresistance ratios without further assumptions. Because of the experimental difficulties with the transverse measurements, however, we have to assume in our case that at very high stress values the (111) conduction band valleys are sufficiently pushed apart so that effects of the stress inhomogeneities are unimportant. We then obtain for the mobility anisotropy in As-doped germanium $K(1) = 6 \pm 0.5$ and $K(2) = 5 \pm 0.6$ for the one and two valley cases, respectively. These values are considerably higher than $K(4)$ of Koenig and Katz⁵ but much lower than a value obtained earlier⁸ from an analysis of these data based on the simple degenerate model with intervalley scattering and the assumption that K is independent of the number of valleys.

Because the resistivity remains a second-rank tensor at all values of stress, one can obtain the principal axes of the mobility tensor μ_{11} and μ_{\perp} for the one and two valley cases from the high stress longitudinal and transverse measurements without further assumptions. These values are shown in Fig. 8 as a function of donor concentration. The length of the vertical bars at the ends of the curves represent the error which stems pre-

¹⁹ D. G. Andrianov and V. I. Fistul, *Fiz. Tverd. Tela* **6**, 470 (1964) [English transl.: *Soviet Phys.—Solid State* **6**, 371 (1964)].

²⁰ I. M. Tsidilkovski, V. I. Sokolov, and G. I. Kharus, in *Proceedings of the International Conference on Semiconductor Physics, Paris, 1964* (Academic Press Inc., New York, 1964), p. 387; and V. I. Fistul, E. M. Omelyanovsky, D. G. Andrianov, and I. V. Dahovsky, *ibid.*, p. 371.

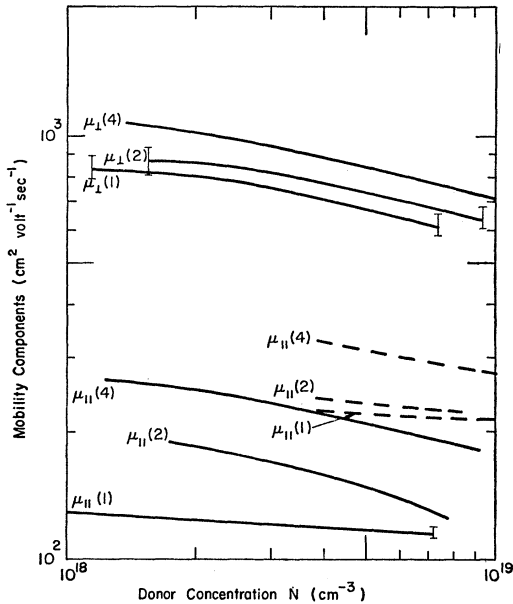


FIG. 8. Mobility components μ_{11} and μ_{\perp} for As donors (full lines) and μ_{11} for Sb donors (dashed lines) as a function of donor concentration at 1.2°K. The bracketed numbers indicate the number of lower conduction band valleys.

dominantly from the uncertainties in the transverse measurements. The mobility components of the four valley case were calculated from the zero-stress mobility. They are subject to the uncertainty of determining the value $K(4)=4.0$ discussed above. The dashed curves in Fig. 8 represent μ_{11} for Sb-doped germanium for which K was found to be $K=3.9\pm 0.1$.

For both As and Sb doping the mobility increases with increasing number of lower valleys. This shows that the increase in mobility due to better screening outweighs the decrease of the mobility due to the lowering of the Fermi energy as the number of valleys is increased from 1 to 4.

Figure 8 demonstrates again the significantly larger scattering experienced by the electrons in the case of As-doping as compared to Sb-doping. This effect is stronger for μ_{11} than for μ_{\perp} , and it is larger for the 1 valley case than for the 4 valley case. This latter observation indicates that the principal cause for the different mobilities in Sb-doped and As-doped Ge cannot be intervalley scattering (caused by the central cell potential of the donors) of the kind discussed earlier⁸ because in that case the mobilities of the one valley case should be nearly equal for the two donor elements.

It should be noted, however, that strong evidence for a considerable contribution of intervalley scattering in As-doped degenerate germanium was observed⁹ in the electronic part of the ultrasonic attenuation at low temperatures. The ratio of intervalley to total scattering time was estimated to be about 10 for As and about 1000 for Sb donors independent of concentration in the range from 10^{18} to 3×10^{19} cm^{-3} .

The size of the central impurity cell potential affects also the intervalley scattering rate. This effect has been discussed by Csavinszky.²¹ He showed that the ratio $\mu(\text{Sb})/\mu(\text{As})$ is expected to be larger than unity and that this ratio increases with increasing impurity concentration because of changes in the screening of the impurity ions in qualitative agreement with the observations (see Fig. 8). A similar result was obtained by Tsidilkovski *et al.*²⁰ who calculated isotropic impurity scattering in the Born approximation using a scattering potential which was matched to the different individual donor ionization energies by a variational method.

It is clear from this evidence that the simple degenerate model, even if amended by intervalley scattering, is incapable of decreasing the piezoresistance effects in As-doped Ge. This conclusion is supported by the observation¹² of an anomalous negative contribution²² to the magnetoresistance effect in this high concentration range. Furthermore, the behavior of interband tunneling in As-doped tunneling junctions shows that in contrast to the case where the donors are Sb the electrons cannot be considered associated with a particular valley.²³ To the donor wave functions, the large central cell potential of the As donors admixes Bloch wave contributions from the other valleys and from other regions of the Brillouin zone, particularly from the region around the zone center. As far as the electrons are shared by all four valleys and by the central minimum, they do not show the expected piezoresistance effects. The similar magnitude of Π_{44} for As and Sb doping indicates that this admixture is relatively small. It depends, however, on the relative energies of the valleys and of the minimum at the zone center and hence it changes with stress. This can give rise to some of the observed changes of the piezoresistance beyond the calculated saturation stress.

Furthermore, some of the tail states may be sufficiently localized to cause a broad resonance scattering of the Breit-Wigner type as the stress moves these tail states past the continuum states near the Fermi level of the lower valley. This affects both the scattering probability and through a change of density of states at the Fermi level the screening of the scattering impurities. If the scattering to these tail states is stronger than intervalley scattering among four degenerate valleys then the larger ratio $\mu_{11}(\text{Sb})/\mu_{11}(\text{As})$ observed for the 1-valley case as compared to the 4-valley case can be understood.

IV. SUMMARY AND CONCLUSIONS

The different effect of As and Sb donors on the transport properties of degenerate germanium becomes

²¹ P. Csavinszky, J. Phys. Soc. Japan, **16**, 1865 (1961).

²² An anomalous positive contribution to the magnetoresistance found in *p*-type Ge seems to be closely related to the negative contribution found in As-doped Ge. See H. Roth, W. D. Straub, and W. Bernard, Phys. Rev. Letters **11**, 328 (1963).

²³ H. Fritzsche and J. J. Tiemann (to be published).

strongly apparent when the material is changed by stress to a 2-valley or a 1-valley semiconductor. In contrast to the case of Sb donors the mobilities of As-doped Ge have a simple power law dependence on concentration in the range $N > 10^{18}$ cm⁻³. They cannot be described by a simple scattering model, however. The presence of an anomalous contribution to the magnetoresistance at these high As concentrations also shows the inadequacy of the simple degenerate model.

The mobility anisotropy factor in As-doped germanium was found to be $K(4) = 4 \pm 0.4$, $K(2) = 5 \pm 0.6$, and $K(1) = 6 \pm 0.5$ for the 4-, 2-, and 1-valley case, respectively. The value $K(2)$ seems to increase and $K(1)$ to decrease slightly as N increases from 10^{18} to 10^{19} cm⁻³.

In contrast to the case of Sb donors the piezoresistance of degenerate As-doped germanium decreases beyond the theoretical saturation stress and approaches a constant value only at very high stresses. This indicates that the presence of localized tail states and their interaction with the valley or valleys shifted down-

wards by stress is more strongly pronounced in As-doped germanium.

The mobility ratio $\mu_{11}(\text{Sb})/\mu_{11}(\text{As})$ is found to be larger for the 1 valley case than for the 4-valley case. This indicates that simple intervalley scattering as discussed earlier⁸ cannot be the primary reason for the lower mobility of As-doped germanium. It is possible, however, that the resonance scattering to the tail states of the valleys which are moved up by the stress is stronger than intervalley scattering among 4 degenerate valleys. Both of these scattering processes are expected to be less for Sb than for As donors because of the large difference in their central cell potentials.

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Behavior of Coherent Microwave Phonons at Low Temperatures in Al₂O₃ Using Vapor-Deposited Thin-Film Piezoelectric Transducers*

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The intrinsic attenuation and velocity of compressional and shear waves have been measured in a single crystal of Al₂O₃ at 1 Gc/sec for *a*-axis propagation. While the slow-shear-mode attenuation shows a T^4 temperature dependence as predicted by the Landau-Rumer theory, the fast shear mode has a T^7 dependence below 50°K and a T^4 dependence at higher temperatures. The compressional mode has a T^9 dependence below 50°K and a T^4 dependence above this temperature. A theory for this behavior is proposed. The measured 300°K velocities are $v_L = 11.03 \times 10^5$, $v_{T_1} = 6.78 \times 10^5$, and $v_{T_2} = 5.72 \times 10^5$ cm/sec. The three plane-wave modes were generated and detected by a single pair of ZnS vapor-deposited thin-film piezoelectric transducers. The crystallographic orientation of the ZnS films relative to the Al₂O₃ was determined by means of reflection electron diffraction and x-ray diffraction. The piezoelectric matrix for ZnS is used to show how independent generation of the three modes was achieved.

INTRODUCTION

THE behavior of the acoustic attenuation in Al₂O₃ at microwave frequencies has been studied by others^{1,2} in an attempt to determine the phonon processes involved. In both cases propagation was directed along the X_3 or *c* axis, which only supports one pure acoustic mode,³ viz., compressional. During the investigation reported here, the acoustic energy was propa-

gated along an X_1 axis. Three pure modes can be propagated along such an axis. Such propagation has been achieved, as reported here, using a single pair of vapor-deposited piezoelectric transducers. Thus, for the first time, it has been possible to determine the intrinsic attenuation behavior of all three pure modes along the same axis and on the same specimen. This enables us to make a valid comparison of the attenuation-temperature characteristics of the three modes as propagation conditions were identical for all three modes.

SAMPLE PREPARATION

Several oriented single-crystal Al₂O₃ rods, 1 in. long by 0.25 in. diameter, were obtained from Linde Com-

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¹ I. S. Ciccarello and K. Dransfeld, Phys. Rev. **134**, A1517 (1964).

² T. M. Fitzgerald, B. B. Chick, and R. Truell, J. Appl. Phys. **35**, 2647 (1964).

³ G. F. Farnell, Can. J. Phys. **39**, 65 (1961).