Valley-Orbit Splitting of Antimony in Germanium*

H. FRITZSCHE

Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received June 23, 1960)

The change of electrical conductivity under uniaxial tension and compression has been measured over the range 4°K to 7°K for single-crystal specimens of germanium doped with antimony. The stress was varied from 1×10^7 to 5×10^8 dynes/cm². On the basis of Price's calculation of the effect of shear on the Kohn-Luttinger donor level structure, an expression for the piezoresistance has been derived, which includes terms of high order in the strain. It is shown that for a finite valley-orbit splitting, i.e., a finite energy separation between the onefold and the threefold 1s-like donor states, shear increases the total electron concentration in the conduction band. For uniaxial stresses along the [110] direction this increase in electron concentration is an even function of stress and can, therefore, be determined from a linear combination of the piezoresistance measured under tension and compression. A comparison of the theoretical expression with the experimentally obtained change in electron concentration yields for antimony in germanium a valley-orbit splitting of 0.57±0.03 milli-electron volt.

I. INTRODUCTION

KOHN and Luttinger's analysis[1] of the energy level structure of group V donors in silicon and germanium shows that all except the ground state can quite accurately be calculated from the hydrogenic model using the effective mass approximation. In this approximation the "1s" donor level[2] is g-fold degenerate (excluding spin degeneracy), where g=4 for germanium[3] and g=6 for silicon, since the donor states are constructed from the Bloch functions of the neighborhood of the g equivalent conduction band minima. Corrections to the effective mass approximation and to the simple Coulomb potential of the donor ion become largest in the immediate vicinity of the donor. The completely symmetrical "1s" state (belonging to the representation A_1 of the tetrahedral group T_d) will be most strongly affected by these corrections because its wave function is the only one with a nonzero amplitude at the donor ion. Because of the attractive potential of the donor ion one expects this state to be lowered in energy with respect to the remaining "1s" donor states, which remain relatively unaffected by the central cell correction. This "1s" splitting energy is called the valley-orbit splitting and will be denoted by $4\Delta_c$.

According to Kohn and Luttinger, the valley-orbit splitting should be roughly the energy difference between the observed activation energy of a particular donor and the ionization energy which is calculated from the hydrogenic model in the effective mass approximation. In several cases, this prediction has been tested by experiment. In germanium the splitting energy was determined for arsenic donors from piezoresistance measurements,[4] for arsenic and phosphorus donors from the strain-induced shifts of the absorption lines of the Lyman series,[5] and for the same elements from the effect of strain on the electron spin resonance.[6] The results are in agreement with one another and with the theoretical predictions. In addition, the valley-orbit splitting was measured for phosphorus in silicon by comparing carrier concentration vs temperature curves derived from the Kohn-Luttinger energy level scheme with experimental curves obtained from Hall data.[7] Agreement with theory was again obtained.

This paper reports the measurement of the valley-orbit splitting of antimony donors in germanium by means of piezoresistance measurements. From the difference between the observed activation energy and the effective mass value one expects for antimony a splitting of about 0.4 milli-electron volt.[1] Because of the small magnitude of the splitting energy, this case requires a somewhat different analysis of the large-strain piezoresistance effect than that used previously for arsenic donors in germanium.

The analysis is based on the following. The presence of the valley-orbit splitting causes the donor activation energy to decrease under the influence of strain. The resultant increase of the total electron concentration is an even function of the shear produced by uniaxial stress along [110]. Since the electron transfer effect is an odd function of the shear for this stress direction, the two processes can be separated by taking the appropriate linear combination of the conductivity changes measured under tension and compression. A comparison of the electron concentration change thus obtained with

---

* Work supported by the U. S. Air Force Office of Scientific Research.

[1] W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

[2] In analogy with the hydrogen atom the donor states can be labeled with the usual notation "1s", "2p," etc.

[3] After this work was completed, E. O. Kane pointed out to me that the currently accepted picture for germanium with 4 equivalent conduction band minima located at the zone face in the [111] directions is not consistent with the existence of 3 and possibly 4 phonons participating in the indirect fundamental optical absorption. Moving the minima to an interior point in the [111] direction would remove this discrepancy. If the minima are indeed inside the zone, then g=8 and the analysis presented in this paper has to be modified. We plan to compare our data with the g=8 model and hope to be able to decide between the two alternatives.

[4] H. Fritzsche, Phys. Rev. 115, 336 (1959).

[5] G. Weinreich and H. G. White, Bull. Am. Phys. Soc. 5, 60 (1960).

[6] D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. 5, 60 (1960).

[7] D. Long and J. Myers, Phys. Rev. 115, 119 (1959).

the value calculated from the shear-induced shifts of the "1s" donor levels yields the valley-orbit splitting.

In the first part of this paper the theory[4] of the piezoresistance effect in n-type germanium is extended to include arbitrary values of the valley-orbit splitting. In the second part, we report measurements of the piezoresistance of antimony-doped germanium as a function of uniaxial stress in the temperature range between 4° and 7°K. In this section the comparison is also made between the experimental results and the theory and the valley-orbit splitting of antimony donors in germanium is computed.

II. THE EFFECT OF VALLEY-ORBIT SPLITTING ON THE PIEZORESISTANCE

We are concerned with strain-induced changes of the electrical conductivity of n-type germanium to higher orders in the strain. Such higher-order terms in the piezoresistance have been examined earlier[4] only for two cases, $4\Delta_c=0$ and $4\Delta_c \gg kT$. In this section the expressions are extended to arbitrary values of $4\Delta_c$.

The discussion is restricted again to $n-$type germanium and to the effect of shear produced by uniaxial stress X in the [110] direction. This treatment is based on basically the same assumptions as the calculations of Herring[8] and Adams.[9]

Choosing for tensile stress positive X and for compressional stress negative X and labeling the conduction band valleys from 1 to 4 according to their axes in the directions [111], [11$\bar{1}$], [1$\bar{1}$1], [1$\bar{1}$$\bar{1}$] in momentum space, we obtain[4] for the shear-induced shifts of the four valleys

$$\epsilon = \epsilon_1 = \epsilon_2 = -\epsilon_3 = -\epsilon_4 = E_2 S_{44} X/6, \qquad (1)$$

where $E_2 \approx 19$ ev per unit strain is the deformation potential for pure shear, and the elastic shear constant[10] is $S_{44}=1.47\times10^{-12}$ cm^2 dyne^{-1}.

We again use $K=\mu_\perp/\mu_{11}$ for the ratio of the electron mobilities perpendicular and parallel to the axis of revolution of a valley and denote the shear-induced shift of the Fermi energy by ϵ_F. One can then write the conductivity change for current and stress along [110] (arrangement C of Smith[11]) as

$$\frac{\Delta\sigma}{\sigma_0}=\left[\frac{K-1}{2K+1}\tanh\left(\frac{\epsilon}{kT}\right)+1\right]\frac{n}{n_0}-1, \qquad (2)$$

where

$$n/n_0=\exp(\epsilon_F/kT)\cosh(\epsilon/kT) \qquad (3)$$

is the ratio of the total electron concentration in the conduction band in the presence of stress to that without stress.

It was shown previously[4] that for zero valley-orbit splitting the total carrier concentration remains independent of the strain, i.e., $n/n_0=1$. In that case the conductivity change is solely due to the electron transfer effect and was found to be

$$\frac{\Delta\sigma}{\sigma_0}=\frac{K-1}{2K+1}\tanh\left(\frac{\epsilon}{kT}\right). \qquad (4)$$

In calculating n/n_0 for finite Δ_c we restrict ourselves to temperatures low enough so that $n \ll N_d - N_a$ and $n \ll N_a$, where N_d and N_a are the donor and acceptor concentrations respectively. Under these conditions the strain-induced shift of the Fermi energy is equal to the shift of the effective donor state energy $E_{d\ \text{eff}}$, which is given by

$$E_{d\ \text{eff}}= -kT \ln\{\sum_l g_l \exp[-(E_d^{(l)}/kT)]\}, \qquad (5)$$

where g_l denotes the degeneracy of the donor state of energy E_d. The sum in Eq. (5) will be extended over the four "1s" states only because the contribution of the higher lying excited states is negligible in the temperature range chosen above. Using the result of Price[12] for the shifts of "1s" donor states as a function of uniaxial stress along [110], one obtains with Eqs. (3) and (5)

$$\frac{n}{n_0}=\frac{1}{2}\cosh\left(\frac{\epsilon}{kT}\right)\frac{3+\exp(4\Delta_c/kT)}{\cosh(\epsilon/kT)+\exp(2\Delta_c/kT)\cosh[(4\Delta_c^2+\epsilon^2)^{\frac{1}{2}}/kT]}. \qquad (6)$$

The valley shift ϵ, as defined by Eq. (1), changes sign from positive to negative when the stress is changed from tension to compression. Since n/n_0 [Eq. (6)] is an even function of ϵ, whereas the electron transfer effect [Eq. (4)] is odd, one can obtain n/n_0 directly from a combination of the conductivity changes measured with tensile and with compressional stress. Using the subscripts X and $-X$ to indicate tension and compression, respectively, one obtains with Eqs. (1) and (2)

$$\frac{n}{n_0}=1+\frac{1}{2}\left(\left.\frac{\Delta\sigma}{\sigma_0}\right|_X+\left.\frac{\Delta\sigma}{\sigma_0}\right|_{-X}\right). \qquad (7)$$

Inserting the experimentally observed n/n_0 in Eq. (6) one can evaluate $4\Delta_c$ without having to determine the mobility anisotropy factor K, which depends in a complicated way on temperature and the scattering processes. Furthermore, when $\epsilon \gg kT$ and $\epsilon \gg 2\Delta_c$, n/n_0 changes very slowly with ϵ. Hence at large stresses, uncertainties in the value of E_2 have a relatively small effect on the determination of the valley-orbit splitting.

Figure 1 shows n/n_0 as a function of Δ_c/kT as calculated from Eq. (6) for various values of ϵ/kT.

III. EXPERIMENTAL DETAILS

Two samples with different antimony concentrations were investigated in order to ascertain whether the

[8] C. Herring, Bell System Tech. J. 34, 237 (1955).
[9] E. N. Adams, Chicago Midway Laboratories Technical Report CML-TN-P3 (unpublished).
[10] M. E. Fine, J. Appl. Phys. 24, 388 (1953).
[11] C. S. Smith, Phys. Rev. 94, 42 (1954).
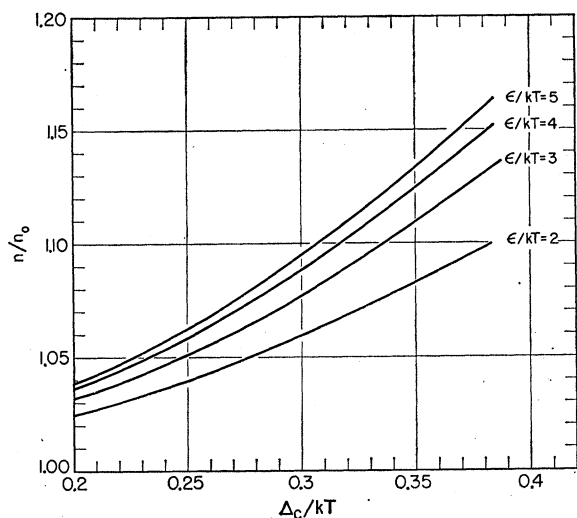[12] P. J. Price, Phys. Rev. 104, 1223 (1956).

FIG. 1. The ratio of the total electron concentration of stressed to that of unstressed germanium as a function of the valley-orbit splitting parameter Δ_c/kT according to Eq. (6) of text.

results are independent of impurity concentration. Sb–1 contained 8.6×10^{13} and Sb–2 contained 5×10^{15} antimony atoms per cc. The compensation ratio was about $N_a/N_d=0.05$. Both samples were single crystals, oriented by x rays to better than one degree, and cut perpendicular to the growth axis to minimize the impurity concentration gradient along their lengths. The
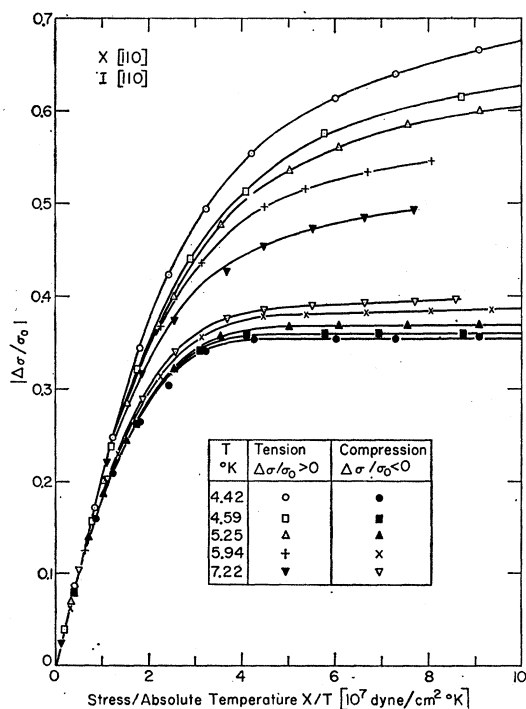

T °K	Tension $\Delta\sigma/\sigma_0>0$	Compression $\Delta\sigma/\sigma_0<0$
4.42	○	●
4.59	□	■
5.25	△	▲
5.94	+	×
7.22	▼	▽

FIG. 2. Relative conductivity changes $\Delta\sigma/\sigma_0$ for current and stress parallel to [110] as a function of uniaxial tensile or compressional stress divided by the absolute temperature.

dislocation density was less than 2×10^3 cm^{-2} in both cases. The sizes, surface treatment and mounting of the samples have been described before.[4] The apparatus was only slightly modified to permit the measurement of the piezoresistance under uniaxial compression as well as under tension. Stresses ranging between 1×10^7 and 5×10^8 dynes/cm^2 were used.

IV. RESULTS AND DISCUSSION

Figure 2 shows for various temperatures the absolute magnitudes of the relative conductivity changes, $\Delta\sigma/\sigma_0$, as a function of uniaxial tensile and compressional stresses along [110]. The current direction is parallel to that of the stress (arrangement C of Smith[11]). For this orientation $\Delta\sigma/\sigma_0>0$ for tension, and $\Delta\sigma/\sigma_0<0$ for compression. The temperatures chosen are low enough so that the conditions $n\ll N_d-N_a$ and $n\ll N_a$ are satisfied. The temperatures were sufficiently high, however, to assure that the conductivity was not affected by impurity conduction. In the case of Sb–1, impurity conduction could not be detected down to the lowest temperatures investigated because of its low impurity concentration. Sb–2 showed the onset of impurity conduction near 5°K, which is much lower than the temperatures used for this sample.

In the following we interpret the difference between the piezoresistance curves of Fig. 2 measured under tension and compression, i.e., the terms in $\Delta\sigma/\sigma_0$ which are an even function of X/T, as being due to a change of the total electron concentration according to Eq. (7). This assumes, however, that there are no disturbing minor effects[13] which are even functions of X.

In order to see whether this assumption is justified we investigated the stress dependence of the still unexplained minor effects which give rise to the small but finite piezoresistance coefficients[4,11] Π_{11} and Π_{12}. These
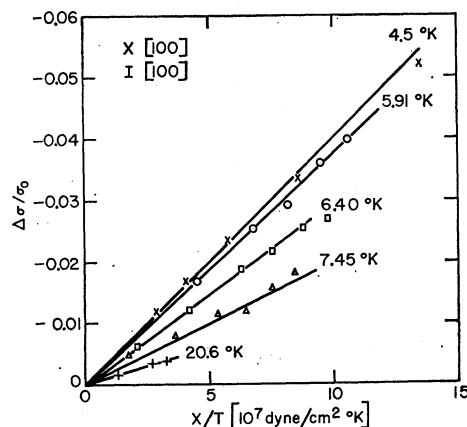

FIG. 3. Relative conductivity changes $\Delta\sigma/\sigma_0$ for current and compressional stress parallel to [100]. The slopes of these curves yield the small piezoresistance coefficient Π_{11} multiplied by the absolute temperature.

[13] F. J. Morin, T. H. Geballe, and C. Herring, Phys. Rev. **105**, 525 (1957).

coefficients can be measured with the stress X and the current I oriented as $X[100]$ $I[100]$ (arrangement A of Smith) and $X[100]$ $I[010]$ (arrangement B), respectively. A linear relationship was found between $\Delta\sigma/\sigma_0$ and X for both cases,[14] which justifies the assumption made above. Figure 3 shows as an example the results for arrangement A using uniaxial compression.

Table I lists for the experimental data obtained with Sb-1 and Sb-2 the result of an analysis based on Eqs. (6) and (7). The values ϵ/kT were calculated from Eq. (1) using a deformation potential $E_2 = 19$ ev per unit shear strain. At each temperature, values of $(\Delta\sigma/\sigma_0 |_X + \Delta\sigma/\sigma_0 |_{-X})$ were obtained from the experimental curves for several values of ϵ/kT to test the functional form of Eq. (6). Equation (7) yields the concentration ratios n/n_0. From these Δ_c/kT was determined for each case using the curves of Fig. 1. Averaging the Δ_c values listed in the last column of Table I, one obtains for the valley-orbit splitting of antimony donors in germanium $4\Delta_c = 0.57 \pm 0.03$ milli-electron volt.

The scattering of the Δ_c values which were determined at different temperatures and stresses is remarkably small. This seems to indicate again that the even-order terms of minor effects, which were not considered in the above analysis, are indeed negligible. A further confirmation of the correctness of our analysis is the fact that, despite the difference in antimony concentrations
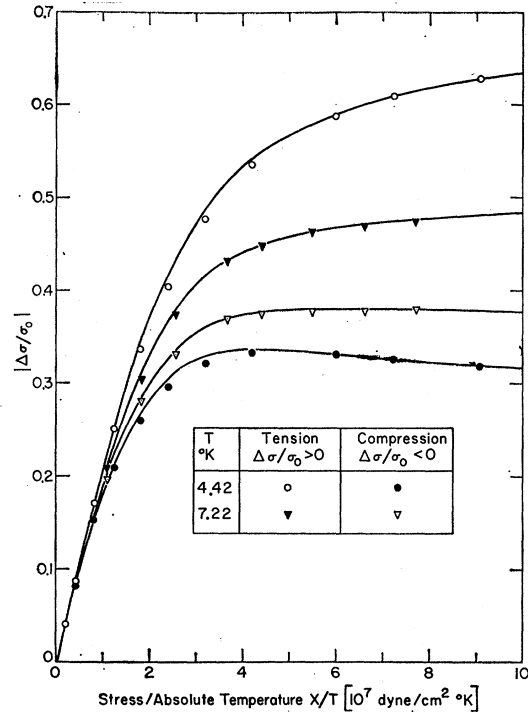

FIG. 4. Comparison of the experimental data with the theoretical curves according to Eqs. (2) and (6) of text using $E_2 = 19$ ev/strain and $4\Delta_c = 0.57$ milli-electron volt. The experimental points have been corrected by subtracting $\frac{1}{2}(\Pi_{11} + \Pi_{12})X$ from the original measurements.

TABLE I. Analysis of the piezoresistance measurements.

Sample	T °K	$\dfrac{\epsilon}{kT}$	$\dfrac{\Delta\sigma}{\sigma_0}\Big|_X + \dfrac{\Delta\sigma}{\sigma_0}\Big|_{-X}$	$\dfrac{n}{n_0}$	Δ_c 10^{-4} ev
Sb-1	4.42	5	0.32	1.16	1.45
		4	0.30	1.15	1.45
		3	0.26	1.13	1.44
	4.59	5	0.266	1.133	1.40
		4	0.24	1.12	1.37
		3	0.22	1.11	1.39
	5.25	5	0.235	1.117	1.49
		4	0.22	1.11	1.50
		3	0.19	1.095	1.49
	5.94	4	0.16	1.08	1.47
		3	0.143	1.071	1.48
	6.41	4	0.117	1.058	1.38
		3	0.104	1.052	1.38
	6.71	4	0.118	1.059	1.45
		3	0.10	1.05	1.43
	7.22	4	0.098	1.049	1.43
		3	0.087	1.043	1.44
Sb-2	7.14	3	0.095	1.048	1.48

of almost two orders of magnitude, the same Δ_c value was obtained for Sb-1 and for Sb-2. An independent check of these results would be the measurement of the Hall coefficient as a function of uniaxial stress. This has not yet been done.

Only the differences between the absolute magnitudes of $\Delta\sigma/\sigma_0$ measured under tension and compression were needed to evaluate Δ_c. If one wants to compare the experimental data with the complete expressions of Eqs. (2) and (6) however, one has to assume a value for the mobility anisotropy K and correct for the minor effects,[4] which give rise to Π_{11} and Π_{12}. The result of such a comparison is shown for the data obtained with Sb-1 and at 4.42°K and 7.22°K in Fig. 4. The experimental points plotted in Fig. 4 were corrected by subtracting $\frac{1}{2}(\Pi_{11} + \Pi_{12})X$ from the original measurements shown in Fig. 2. The best fit of the theoretical curves in Fig. 4 with the corrected data was obtained by choosing for the mobility anisotropy the value $K = 7.8$. This value is in good agreement with previous piezoresistance[4] and magnetoresistance measurements.[15]

In the above treatment of the donor states, particularly in connection with Eq. (5), it was assumed that the donor levels have a well-defined, sharp energy. Lax

---

[14] This disagrees with measurements on arsenic-doped germanium where a small second-order effect was observed for arrangements A and B (see reference 4). No explanation is presently known for this discrepancy.

[15] C. Goldberg, Phys. Rev. 109, 331 (1958); C. Goldberg and W. E. Howard, Phys. Rev. 110, 1035 (1958); R. A. Laff and H. Y. Fan, Phys. Rev. 112, 317 (1958).

TABLE II. Valley-orbit splitting energies of
group V impurities in germanium.

Impurity element	E_d(obs) − E_d(eff mass)[a] milli-electron volts	$4\Delta_e$ milli-electron volts
P	2.8	3.0 ±0.3[b]
		2.9 ±0.2[c]
As	3.5	4.1 ±0.15[d]
		3.9 ±0.6[b]
		4.2 ±0.2[c]
Sb	0.4	0.57±0.03
Bi	0.1	

[a] E_d(obs) values were taken from J. A. Burton, Physica **20**, 845 (1954); E_d(eff mass) =9.2 milli-electron volts (see reference 1).
[b] See reference 5.
[c] See reference 6.
[d] See reference 4.

and Burstein,[16] however, explained the width of the infrared absorption lines in silicon at low temperatures as a finite broadening of the impurity levels from the thermal and zero-point vibrations of the lattice. Inserting the constants appropriate to germanium into their formulas, one finds for the "1s" donor levels a zero-point broadening of about 0.3 milli-electron volt, which corresponds to a temperature of 4°K. Between 4°K and 7°K, the temperature range of our measurements, the broadening would be increased by thermal vibrations to about 0.8 milli-electron volt according to the calculations of Lax and Burstein. With such a large broadening our present analysis of the data would lose all its validity. However, there is an argument[17] which shows that the observed broadening of the infrared absorption lines does not imply that the impurity levels themselves are broadened.

In the adiabatic approximation the levels of an isolated impurity atom are sharp because they are the energy eigenstates of the Hamiltonian of the system which includes the adiabatic interactions of the electron with the lattice vibrations in addition to the attractive potential of the impurity ion and the periodic lattice potential. At high impurity concentrations the levels are broadened by the interaction of the randomly distributed impurities. The electron-lattice interaction changes the energy eigenstates of the system with respect to their values in a perfectly periodic lattice. The phonon spectrum itself is also modified by an amount which is proportional to the impurity concentration and hence negligible in our case. However, if the adiabatic approximation is not valid, the nonadiabatic terms will mix the adiabatic states and hence give rise to a lifetime broadening.

The adiabatic approximation seems to be justified in

[16] M. Lax and E. Burstein, Phys. Rev. **100**, 592 (1955).
[17] I am very grateful to M. H. Cohen for pointing this out to me.

the case of arsenic impurities for which the valley-orbit splitting is large compared to the energy of the most effective phonon, that with wavelength equal to the radius of the ground state orbit. This phonon energy, however, is of the same order of magnitude as the valley-orbit splitting of antimony impurities. How the breakdown of the adiabatic approximation affects the energy states of antimony impurities is presently being investigated.[18]

Because of the electron-phonon interaction, in each of the sharp energy eigenstates of the system the electron and phonon coordinates are mixed. Thus in an interaction between an electron and an electromagnetic field phonon emission and, at finite temperatures, phonon absorption are possible. This will be one source of broadening of the infrared absorption lines.

Table II summarizes the valley-orbit splitting energies of various group V impurities in germanium. The values estimated from the differences between the observed activation energies and the activation energy which is obtained from the effective mass approximation are listed in the second column. The results of direct measurements of the valley-orbit splittings shown in the third column are consistently larger than those obtained from the activation energies. This is to be expected since the presence of the three-fold "1s" state causes the effective donor activation energy to be slightly smaller than the energy separation between the "1s" ground state and the conduction band edge.

V. SUMMARY

With the assumption that the relative population changes of the different conduction band valleys and the effective donor activation energy are the only effects of the shearing strain, Eqs. (2) and (6) have been derived, which give the effect of uniaxial [110] stress on the electrical conductivity as a function of stress and the valley-orbit splitting energy. These expressions are based on the four-valley model of germanium and are valid at low temperatures where $n \ll N_d - N_a$ and $n \ll N_a$. The valley-orbit splitting can be obtained from a linear combination of the $\Delta\sigma/\sigma_0$ values measured under tension and compression along the [110] direction. The advantage of this method is that it is independent of the mobility anisotropy of the valleys. The valley-orbit splitting of antimony in germanium was found to be $4\Delta_e = 0.57 \pm 0.03$ milli-electron volt in good agreement with the Kohn-Luttinger theory.

[18] *Note added in proof*. W. D. Twose of our laboratory calculated the lifetime broadening of the threefold 1s-like donor state at temperatures near 7°K. He found a broadening of 3×10^{-6} ev for arsenic and 2×10^{-5} ev for antimony donors in germanium. His calculation is in essence the same as that of E. O. Kane, Phys. Rev. **119**, 40 (1960). It appears that our analysis of the piezoresistance is justified because the broadening is much smaller than the valley-orbit splitting for both kinds of impurities.