

when one determines ensemble averages of the spin operators, thereby summing over all states, those relatively few states for which the matrix elements of $\rho(t)$ do not have "typical" behavior, could be expected to be unimportant.

The diagonal singularity condition still holds under the assumption of random signs. One finds that $\langle \theta | V^2 | \theta \rangle$, $\langle \theta | V^2 | j \theta \rangle$, $\langle \theta | V^2 | j k \theta \rangle$, $\langle \theta | V^2 | j k m \theta \rangle$, and $\langle \theta | V^2 | j k m n \theta \rangle$ are of order N^2 , N , N , $N^{1/2}$, and 1, respectively. In order that the $\lambda^2 t$ contributions not be made negligible as $N \rightarrow \infty$, it must also be true that $\langle \theta | V^2 | \theta \rangle$ is of the same order as $\sum_{\theta'} \langle \theta | V^2 | \theta' \rangle$. That this is true is readily verified.

With these results, the rate equations may be obtained in a manner similar to that in the preceding section, and we need not repeat the details. One obtains precisely the same equations for $\langle \theta | \rho(t) | \theta \rangle$ and $\langle \theta | \rho(t) | j \theta \rangle$ as by the earlier considerations of this section involving use of the partial random phase assumption on the initial density matrix elements.

IV. DISCUSSION

For each of the perturbations considered in this paper, we have obtained in the weak-coupling, long-time approximation, Pauli equations for the diagonal density matrix elements, and equations of the type (9) for the off-diagonal elements. For the random perturbation of Sec. II, no initial random phase assumption was needed in the derivation of these equations. A partial random phase assumption, in the case of spin-spin interactions, was shown to be a sufficient condition for obtaining these equations. Alternately, it was shown, for spin-spin interactions, that no initial statements need be made about the density matrix elements, if one accepts the assumption that the phases in the perturbation matrix elements can be treated as random.

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Effect of Elastic Strain on Interband Tunneling in Sb-Doped Germanium*

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The effects of uniaxial compression and of hydrostatic pressure on the direct and indirect tunneling processes in germanium tunnel diodes have been studied experimentally under forward and reverse bias at 4.2°K and compared with Kane's theory. The diodes were formed by alloying indium doped with $\frac{3}{8}\%$ gallium on (100) and (110) faces of germanium bars containing an antimony concentration of $5.5 \times 10^{18}/\text{cm}^3$. The first order change of the tunneling current with stress was measured at fixed bias voltages. For biases smaller than 8 mV the current is direct and not affected by the relative shifts of the (111) conduction band valleys. In the bias range of indirect tunneling the anisotropic tunneling from the (111) valleys was observed in agreement with theory. In the range of direct tunneling to the (000) conduction band the current change is correlated with the stress induced change of the direct band gap and of the energy separation between the (111) and (000) conduction bands. This separation was found to be 0.160 ± 0.005 eV at zero stress in agreement with optical measurements on degenerate germanium. Some details of the bias dependence of the pressure effect including some fine structure at small biases remain unexplained.

I. INTRODUCTION

AS a result of extensive experimental and theoretical efforts, the main features of the tunneling process in Esaki tunnel diodes¹ have been clearly established. However, since it is difficult to assess the validity of some of the simplifying assumptions and approxima-

tions which underlie our present theoretical understanding of this process, it is not clear to what extent the existing theories^{2,3} should explain the finer details of the experimental observations. This problem is particularly difficult to resolve because tunnel diodes can only be made in highly impure materials. This fact

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¹ L. Esaki, Phys. Rev. **109**, 603 (1958).

² L. V. Keldysh, Soviet Phys.—JETP **6**, 763 (1958); **7**, 665 (1958); W. Franz, Z. Naturforsch. **14a**, 415 (1959); E. O. Kane, J. Phys. Chem. Solids **12**, 181 (1959); P. J. Price and J. M. Radcliffe, IBM J. **3**, 364 (1959); W. P. Dumke, P. B. Miller, and R. R. Haering, J. Phys. Chem. Solids **23**, 501 (1962).

³ E. O. Kane, J. Appl. Phys. **32**, 83 (1961).

precludes the possibility of ever performing a tunnel diode experiment under very ideal conditions. It is hoped that some of these difficulties can be alleviated by performing a series of experiments upon each diode. In this paper we discuss measurements of the effect of hydrostatic pressure and of uniaxial compression on the tunneling current of germanium tunnel diodes at helium temperatures. A subsequent paper will report the temperature dependence of the tunneling current of the same diodes.

The effects of elastic strain will strongly depend on the effective-mass anisotropies and on the deformation potentials of the relevant band extrema. Most of these quantities are known for germanium.⁴ Furthermore, in germanium, two types of tunneling have been observed,^{5,6} and theoretical expressions for both types have been derived.³ These two tunneling processes are (1) direct tunneling and (2) indirect or phonon-assisted tunneling. The relative proportion of the current carried by these two processes depends on the temperature, the bias voltage, and on whether As, P, or Sb is used as the donor impurity.⁵ Although the mechanism is not understood theoretically at present, direct tunneling predominates in As- and P-doped diodes at all temperatures and biases. In Sb-doped diodes, on the other hand, one observes at helium temperatures several distinct bias regions in which one or the other of these processes is dominant. This material has the advantage that both direct and indirect tunneling are observable in separate bias ranges in a single diode.

This is important because there is considerable experimental uncertainty as regards the details of the impurity distribution within the junction itself. By measuring both types of tunneling in one sample, this uncertainty does not affect the conclusions. Antimony-doped germanium tunnel diodes have the additional advantage that the unambiguously direct tunneling to the (000) minimum in the conduction band is much more clearly observed.^{6,7}

The main effect of elastic strain on the tunneling current arises from the shifts in energy of the conduction band valleys with respect to the valence band. Hydrostatic pressure causes all of the conduction band valleys to rise in energy, but the (000) valley moves faster than the (111) valleys.⁸ In addition, shear stress can shift the (111) valleys with respect to one another.⁹ These effects can be quantitatively calculated by applying

⁴ R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. II, p. 149.

⁵ N. Holonyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, *Phys. Rev. Letters* **3**, 167 (1959); Y. Furukawa, *J. Phys. Soc. Japan* **15**, 1903 (1960); R. N. Hall, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960*, (Czechoslovakian Academy of Sciences, Prague, 1961), p. 193.

⁶ J. V. Morgan and E. O. Kane, *Phys. Rev. Letters* **3**, 466 (1959).

⁷ R. N. Hall and J. H. Racette, *J. Appl. Phys.* **32**, 2078 (1961).

⁸ W. Paul, *J. Phys. Chem. Solids* **8**, 196 (1959).

⁹ C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).

deformation potential theory to the expressions for the tunnel current derived by Kane.³ The calculated behavior is in good qualitative agreement with the main features of the experimental data.

II. THEORETICAL CONSIDERATIONS

According to Kane's theory,³ the tunneling current flowing from a single valley in the conduction band to the valence band is given by

$$I_d = C_d D_d \exp(-\alpha) \quad \text{with} \quad \alpha = \lambda_d E_g^{3/2} m^{*1/2} / F, \quad (1)$$

when the transition is direct, i.e., when the conduction and valence band extrema occur at the same wave number \mathbf{k} . It is given by

$$I_i = C_i D_i \exp(-\beta) \quad \text{with} \quad \beta = \lambda_i (E_g \pm \hbar\omega)^{3/2} m^{*1/2} / F, \quad (2)$$

when the transition is indirect, i.e., when the band extrema occur at different \mathbf{k} . In Eq. (2) $\hbar\omega$ is the energy of the phonon needed to conserve wave number in the tunneling process. The upper sign is for p to n tunneling (reverse bias), the lower sign for n to p tunneling (forward bias).

In Eqs. (1) and (2), E_g is the appropriate band gap; $m^* = (1/m_{hx} + 1/m_{ex})^{-1}$ is the reduced effective mass in the tunneling direction. The quantities C and λ are given by Kane. The average junction field is given by

$$F = [2\pi n^* (E_g + \zeta_n + \zeta_p - eV) / \kappa]^{1/2}, \quad (3)$$

where $n^* = np / (n + p)$ is the reduced doping constant, κ is the dielectric constant, ζ_n and ζ_p are the Fermi level penetrations into the conduction band and the valence band, respectively, and E_g is the smallest band gap. The phonon energy has to be considered also in the density of states factor D_i as will be discussed later. The density of states factor is given in Kane's notation by

$$D = \int [1 - \exp(-2E_g / \bar{E}_1)] [f_1(E_1) - f_2(E_2)] dE. \quad (4)$$

When there is more than one valley in the conduction band, or more than one valence band, the total current will be a sum over all combinations of conduction band and valence band extrema which can contribute. Because of the exponential dependence on the reduced mass appearing in Eqs. (1) and (2), however, this sum for germanium can be reduced to only those transitions which involve the light hole band. Furthermore, since the conduction band valleys in germanium are quite anisotropic, and since the tunneling probability depends only on the effective mass along the direction of tunneling,¹⁰ the current contributions of the four (111) valleys will, in general, be different.

¹⁰ The tunneling direction for isotropic effective masses is along the direction of the electric field (perpendicular to the plane of the junction). For an anisotropic effective mass, the tunneling direction lies between the electric field direction and the direction of minimum effective mass. We have assumed that in all cases the tunneling direction coincides with the electric field; so we have slightly overestimated the nonequivalence of the valleys.

That part of the applied stress which is associated with a volume change affects the tunnel currents primarily through E_g and m^* , which appear in the exponents of Eqs. (1) and (2). The variations of these quantities with stress can be estimated from the known pressure coefficients of the band gaps.

The pure shear part of the stress causes the conduction band valleys to shift in energy with respect to one another in such a way that their average energy is unchanged. Therefore, for the shifts in valley energies to produce a current change which is linear in stress, it is necessary (a) that the degeneracy of the valleys be removed by shear, and (b) that the current contributions of the valleys which are raised in energy be unequal to the contributions from those which are lowered.

If the electric field is in a $[100]$ direction, all (111) valleys have the same effective-mass component in the field direction. For such a diode an energy shift of the valleys should not produce a current change which is linear in shear stress.¹¹ If the electric field is in the $[110]$ direction, however, two valleys (those along $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$) have reduced effective masses along the field direction $m_1^* = m_2^* = (1/m_{te} + 1/m_h)^{-1} = 0.027 m_0$; while the two other valleys (along $[111]$ and $[1\bar{1}\bar{1}]$) have reduced effective masses $m_3^* = m_4^* = (1/3m_{te} + 2/3m_{te} + 1/m_h)^{-1} = 0.034 m_0$, where m_{te} , m_{te} , and m_h are the principal electron masses and the light-hole mass, respectively. Even though these effective masses differ by only about 25%, the currents themselves will differ by a large factor because of the exponential dependence. In our samples, for example, the exponent is about equal to 17. This leads to a factor of 6 difference in the currents. Such a diode will exhibit a first-order stress coefficient for a shear which causes the similar valleys to move in the same direction. (On the other hand, a shear which raises one valley of each pair while lowering the other valley will have no first-order shear dependence.)

III. EXPERIMENTAL

Our experimental diodes were chosen so that they are as identical as possible except that one sample has the electric field along the $[001]$ axis and the other along $[110]$. For both samples the uniaxial stress direction was $[110]$. The samples were in the form of rectangular bars with the long dimension along $[1\bar{1}0]$ and the short dimensions along $[110]$ and $[001]$. Two diodes were alloyed near the center of each bar on opposite faces. It was found to be necessary to do this because it was impossible to avoid flexing the bars slightly. Since flexure causes equal and opposite stresses on

¹¹ There is another mechanism by which shear can produce a first-order effect. In addition to a change in the valley energy, shear causes a deformation of the effective mass ellipsoids. Since tunneling depends only on the projection of the effective mass along the direction of tunneling, rather than an average over all directions, a linear effect occurs. This effect operates even when the valley in question is at a point of symmetry such that the valley energy cannot depend on shear.

opposite faces, the average of the results obtained from these diodes is independent of flexure.

The starting material was pulled along the $[110]$ axis from a melt containing 6% Sb by weight. After orientation by x rays, the crystal was cut into wafers. These wafers were reoriented and cut into bars with the long dimension along $[1\bar{1}0]$ and the short dimensions along $[110]$ and $[001]$. From resistivity and Hall effect measurements, the Fermi level penetration of our samples was calculated to be $\zeta_n = 0.020 \pm 0.002$ V. The diodes were formed by alloying indium dots doped with 3/8% gallium on the appropriate faces. Double contact wires were attached to the dots and the samples were etched to remove the perimeter of the junctions. (This was done because the perimeter has the wrong orientation.) The diameter of a typical diode dot was about 0.05 cm.

The Fermi level on the p -type side was estimated to be approximately 0.140 ± 0.020 eV. No direct measurements were made to confirm this estimate, but since none of our conclusions is sensitive to the choice of ζ_p , as long as $\zeta_p > \zeta_n$, the accuracy of the estimate is unimportant.

Uniaxial compressional stresses X varying between 5×10^7 and 5×10^8 dyn/cm² were applied parallel to the $[1\bar{1}0]$ direction at temperatures between 1.5 and 4.2°K. The stress tunneling coefficient defined as $\Pi = \Delta I / IX$ averaged over the two opposed diodes was found to be independent of stress and of temperature within these ranges. The stress tunneling coefficients were measured at fixed bias voltages. In order to minimize the effect of series resistances due to the leads and the sample, the bias was measured potentiometrically using one pair of the double contact wires attached to the diode and to an Ohmic contact in close proximity of the diodes while the current was passed through the other pair of contact wires. Liquid helium was used as the pressure transmitting fluid for the hydrostatic pressure measurements. These were extended up to $p = 10^3$ psi.

Figure 1 shows the stress tunneling coefficient as a

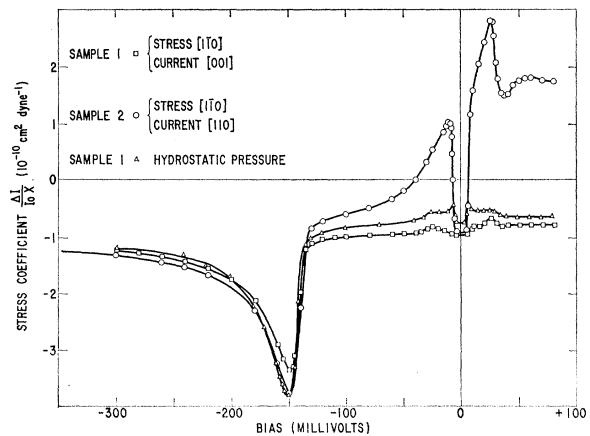


Fig. 1. Stress coefficients for uniaxial $[1\bar{1}0]$ compression and hydrostatic pressure as a function of bias voltage at 4.2°K.

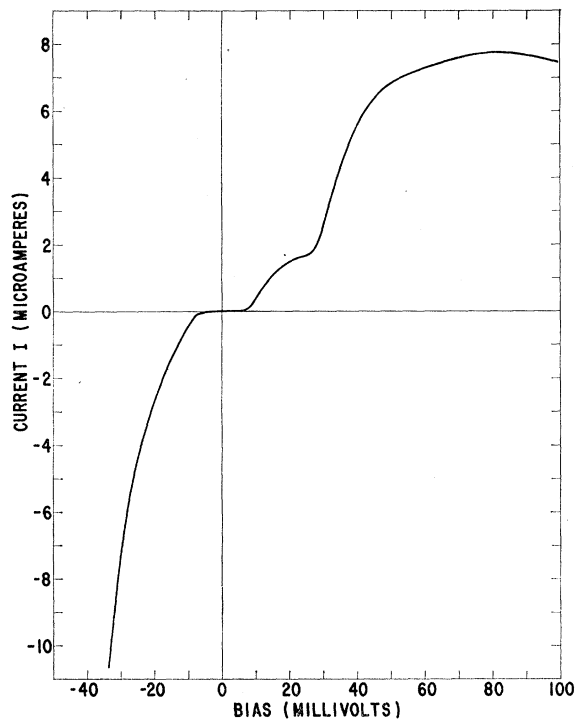


FIG. 2. Current-voltage characteristic of one diode of sample 2 at 4.2°K. Note the onsets of the *TA* and *LA* phonon contributions near the bias voltages ± 8 and ± 28 mV, respectively.

function of bias for the two samples. In sample 1 the diodes are on the (001) faces. This sample should, therefore, not respond to the shear induced shifts of the conduction band valleys. In sample 2 the diodes are on the (110) faces. The difference between these two curves is due mainly to the nonequivalence of the two pairs of valleys for tunneling in the $[110]$ direction and the fact that the shear part of the applied stress causes these pairs to move in opposite directions.

The same figure shows the hydrostatic pressure coefficient of sample 1 at 4.2°K. In order to make a direct comparison with the uniaxial compression data possible $\Pi_p = \Delta I / I_3 p$ was plotted. The difference between the uniaxial and the hydrostatic pressure coefficients of sample 1 is due to the shear-induced effective mass changes of the electrons and light holes in the tunneling direction.

The I - V characteristic of one of the diodes of sample 2 is plotted on Fig. 2. The two diodes were so closely matched that their characteristics did not differ by more than 10% over the whole voltage range. The characteristic has the shape typical for indirect tunneling.⁵ Only a very small current can flow until the bias is large enough to permit the emission of a low-energy phonon needed for wave number conservation in the tunneling process from a (111) conduction band valley to the (000) valence band. The current increases again when a higher energy phonon of the same wave number can be emitted. The phonons have been identified pre-

viously⁵ as the *TA* and *LA* $[111]$ phonons which have the energies 0.0076 and 0.028 eV, respectively.¹²

The I - V characteristic of the same diode is plotted on a different scale in Fig. 3 in order to show the rapid increase of the reverse current at a bias voltage of about -140 mV. This so-called Kane kink occurs⁶ when the back bias is large enough to move the higher lying conduction band edge at $k=0$ on the *n*-type side below the Fermi level in the valence band on the *p*-type side, and thus, to allow a large direct tunneling current to flow. The relative position of the bands is shown schematically in Fig. 4 for a reverse bias beyond the Kane kink.

IV. INTERPRETATION

Comparing Figs. 1 and 2 one sees that the stress coefficients Π of the two samples differ greatly in the bias range of indirect tunneling, i.e., for $-135 < V < -8$ mV and $V > 8$ mV. We shall interpret this difference as being due to the shear induced shifts of the (111) valleys and the nonequivalence of the two pairs of valleys for tunneling in the $[110]$ direction. In the small bias range $-8 \text{ mV} < V < +8 \text{ mV}$ a very small current flows. This must be due to a direct tunneling process since the energy difference between the Fermi levels on the *n*-type and *p*-type sides is too small for the emission of a phonon. Although the detailed nature of this direct tunnel current is not known, the relative magnitude of this component in Sb-, P-, and As-doped germanium tunnel diodes indicates⁶ that the origin of this direct process is related to the impurity cell potentials of the *n*-type impurities.¹³ The fact that the stress coefficients of the two samples are practically identical in this range indicates furthermore that this direct tunneling process cannot be associated with the density of states and the band edge energies of the individual (111) valleys.

As can be seen from Fig. 1, both samples exhibit a sharp rise in the stress coefficient at about 140-mV reverse bias. This effect is obviously associated with the onset of direct tunneling into the (000) conduction band. All three curves are nearly the same beyond the Kane kink. This one expects since the (111) valley contribution to the current is negligible in this range.

In the following we shall attempt a quantitative comparison between the experiments and Kane's theory.

¹² There is additional structure due to the optical phonons. Since this structure is small, we have treated the contribution of these phonons together with that of the higher energy acoustic phonon.

¹³ The impurity cell potentials give rise to an admixture of (111) and (000) conduction band states to the wave function of a given electron and hence permit a fraction of the current to flow without phonon participation. Since these impurity cell potentials give rise also to the valley-orbit splittings of the $1s$ -like states of isolated Group V donor impurities one expects the relative strength of this phonon unassisted current for the different donor elements to correlate with the magnitude of this splitting. It may be misleading to refer to this process as direct tunneling since one is not dealing with an electron wave function characterized by the wave number $k=0$. We use the term only to denote that no phonons participate in the process.

1. Stress Tunneling Coefficient Beyond the Kane Kink

One expects the onset of direct tunneling to the (000) conduction band to occur at a reverse bias voltage

$$V_k = -[E_g(000) - E_g(111) - \zeta_n]/e. \quad (5)$$

Since the pressure coefficient for the direct gap $E_g(000)$ is larger than that for the indirect gap $E_g(111)$,⁸ that part of the uniaxial compression X which corresponds to a hydrostatic pressure $p = X/3$ causes the onset voltage V_k to increase. This results in an anomalously large negative value of $\Delta I/I$. As one goes to higher reverse bias, this contribution becomes relatively unimportant and the stress coefficient approaches the value determined by the stress-induced changes of $E_g(000)$ and the combined electron and hole effective mass $m^*(000)$. Figure 1 shows that these changes are determined mainly by the hydrostatic pressure part of the stress. The shear part does not change $E_g(000)$. It deforms, however, the effective mass spheres, which gives rise to a small contribution which is different for the two diode orientations.

Beyond the Kane kink the tunnel current is the sum of the direct current I_d and the indirect current I_i (see Fig. 4). Following Kane one has

$$I_d = C_d D(V - V_k) \exp(-\alpha), \quad (6)$$

with

$$\alpha = \lambda_d E_g^{3/2}(000) m^*(000)^{1/2} / F, \quad (7)$$

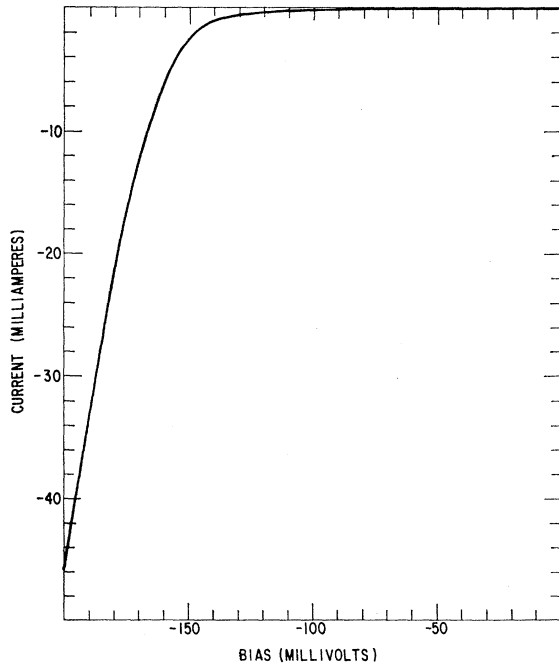


FIG. 3. Current as a function of reverse bias of one diode of sample 2 at 4.2°K. Note the sharp increase in current near $V = -140$ mV.

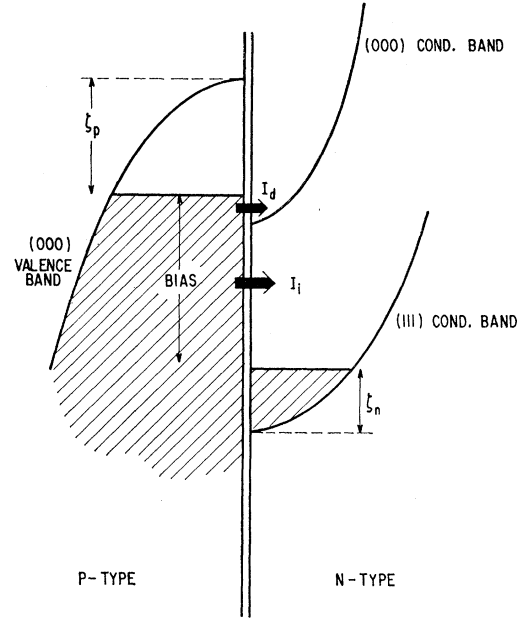


FIG. 4. Relative position of the bands and Fermi levels in a germanium tunnel diode for a reverse bias beyond the Kane kink.

and

$$D(V - V_k) = e(V - V_k) + \frac{E_g(000)}{4\alpha} \left\{ 1 - \exp\left[\frac{4\alpha e}{E_g(000)} (V - V_k) \right] \right\}. \quad (8)$$

The relative change of the tunnel current is

$$\Delta I/I = (\Delta I_d + \Delta I_i) / (I_d + I_i). \quad (9)$$

It can be seen from Fig. 4 that beyond the Kane kink the indirect current is an appreciable fraction of the total current only over a small bias range. For the purpose of explaining the data we can, therefore, use for I_i and ΔI_i in Eq. (9) the extrapolations of the indirect current curves into the bias range beyond the Kane kink.

For the change of the direct current one obtains from Eqs. (6) and (7), neglecting the relatively minor change of C_d ,

$$\Delta I_d = I_d \frac{1}{D} \frac{dD}{dV_k} - I_d \alpha \left[\frac{3}{2} \frac{\Delta E_g(000)}{E_g(000)} + \frac{1}{2} \frac{\Delta m^*(000)}{m^*(000)} - \frac{\Delta F}{F} \right]. \quad (10)$$

The first term in Eq. (10) is responsible for the sharp maximum of the stress coefficient near V_k , and the second term determines its asymptotic value at large reverse bias. The quantity ΔV_k is

$$\Delta V_k = -(\Xi_{000} - \Xi_{111})X/3, \quad (11)$$

where $\Xi_{000} = 12 \times 10^{-12}$ Vcm²/dyn and $\Xi_{111} = 5 \times 10^{-12}$ Vcm²/dyn are the pressure coefficients for the direct and the indirect band gap, respectively.⁸

Before one can calculate the theoretical bias dependence of the stress coefficient, it is necessary to estimate α and the value of $\Delta m^*(000)/m^*(000)$. The shear contribution to the latter quantity depends on the field direction and hence is different for our two samples. Its magnitude cannot be obtained without knowing the various deformation potentials which determine the stress-induced changes of the effective mass tensors at the zone center. Figure 1 shows, however, that the shear contribution is small. The relative change of the reduced mass caused by the hydrostatic pressure can be estimated from

$$\Delta m^*(000)/m^*(000) = \Delta E_g(000)/E_g(000), \quad (12)$$

since the masses involved are mainly determined by the interaction between the light hole band and the conduction band at the zone center.¹⁴ The quantity α was then determined by fitting Eq. (10) and the experimental hydrostatic pressure curve of sample 1 at large reverse bias. From this fit, the value $\alpha = 17.6$ was obtained for $V = -300$ mV.

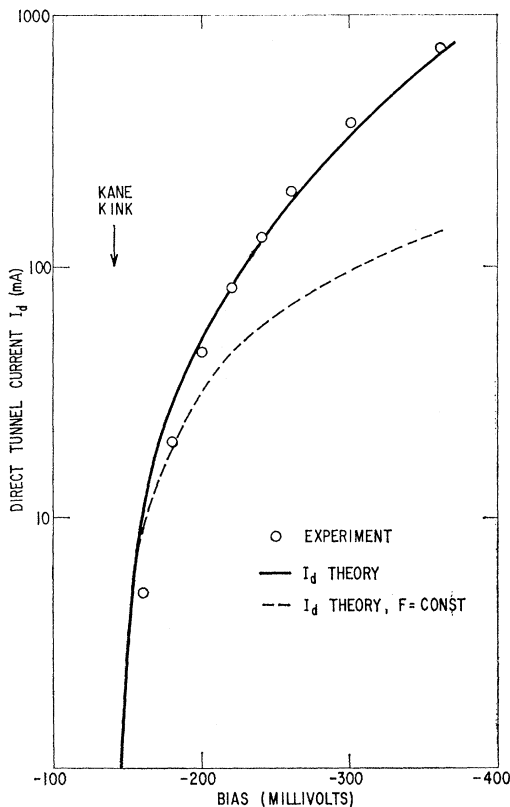


FIG. 5. Comparison between theory and experiment of the bias dependence of the direct tunnel current beyond the Kane kink. The factor C_d of Eq. (1) (see text) has been chosen to fit the absolute magnitude of the theoretical and experimental I_d near -220 mV reverse bias.

¹⁴ E. O. Kane, J. Phys. Chem. Solids **7**, 249 (1957). For the relationship between effective masses and energy gap, see also H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).

As an independent check, the bias dependence of the direct tunnel current itself was compared with Eqs. (6) and (7) using this α . The comparison with experiment is shown in Fig. 5. The constant factor C_d of Eq. (6) was chosen to fit the magnitudes of the measured and the calculated current. It is seen that this value of α predicts the shape of the I - V characteristic quite well. This agreement was not noted by Morgan and Kane⁶ because they assumed the junction field F did not change with bias. Even though F varies by only about 10%, the value of the exponential factor varies by a factor of 6 over the bias range of interest.

The theoretical stress coefficient is compared with experiment in Fig. 6. It is seen that there is good qualitative agreement except that the theoretical maximum is sharper than the experimental curve. There are several effects which will cause a smearing out of the theoretical curve. (1) Thermal fluctuation will cause about a 1.5-mV broadening. (2) Random fluctuations of the impurity concentrations on a microscopic scale will cause local fluctuations in ζ_n . These will correspond to a range of V_k values rather than a unique value as was assumed. (3) There may also be a nonuniform built-in stress in the diodes. Since $E_g(000)$ and $E_g(111)$ depend differently on stress, this would also cause a spread in V_k .

For pure germanium $E_g(000) - E_g(111) = 144$ mV.¹⁵ For our samples, V_k should, therefore, occur at 124 mV. The observed V_k is clearly larger than 136 mV. This discrepancy may be due to a depression of the (111) conduction band relative to the (000) conduction band due to the large impurity concentration,¹⁶ or it may be due to a permanent strain at the junction caused by the difference in lattice constant of the n -type and the p -type regions, or possibly by the difference in the thermal expansion coefficient of the dot material and the germanium.¹⁷

2. Stress Coefficient in the Indirect Tunneling Range

Except for the narrow voltage region at zero bias (see Fig. 2) the tunneling is almost entirely indirect for $V_k < V$. In this bias range the stress coefficients of the two samples differ strongly. This difference is due to the fact that in sample 1 all four valleys are equivalent with the respect to the junction field direction, whereas in sample 2 the two pairs of valleys which are shifted with respect to one another by shear have different effective mass components in the field direction.

The difference between the hydrostatic and the uniaxial stress coefficient of sample 1 (see Fig. 1) is due

¹⁵ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Proc. Phys. Soc. (London) **71**, 863 (1958).

¹⁶ C. Haas, Phys. Rev. **125**, 1965 (1962).

¹⁷ It is clear that stresses of sufficient magnitude to account for this discrepancy can easily be encountered unless special precautions are taken to avoid them. For example, S. Zwerdling, B. Lax, L. M. Roth, and K. J. Button [Phys. Rev. **114**, 80 (1959)] measured $E_g(000) - E_g(111) = 0.154$ eV in strained material.

to the shear-induced changes of the effective mass components in the field direction. It is interesting to note that these changes are of appreciable magnitude. We find $(1/m^*)(dm^*/dX) \approx 5 \times 10^{-12}$ cm²/dyn. Since m^* is the reduced mass, we cannot separate the contributions of the light hole mass and of the (111) electron mass. The fact that the shear dependence of the current beyond the Kane kink is quite small allows us to conclude that either the effective mass deformation occurs mostly on the (111) ellipsoids or that there is an accidental cancellation of the deformations of the light holes and the (000) conduction band extremum.

The bias dependence of the hydrostatic pressure coefficient shows a clearly resolved structure at small bias voltages which is almost symmetrical with respect to the forward and reverse bias direction. In the small bias range of direct tunneling the pressure coefficient $\Pi_p = \Delta I / 3I p$ is about $\Pi_p = -7.5 \times 10^{-11}$ cm²/dyn. Π_p changes to $\Pi_p = -4 \times 10^{-11}$ cm²/dyn at $V = \pm 6$ mV before it reaches a constant value in the *TA* phonon region. Introducing for brevity the notation $\Pi_p(TA, \pm V)$ and $\Pi_p(LA, \pm V)$ to represent the pressure coefficient in the *TA* and *LA* phonon regions, at positive and at negative biases, respectively, we can list the experimental values in these regions as follows: $\Pi_p(TA, +V) = -5.3$; $\Pi_p(TA, -V) = -5.7$; $\Pi_p(LA, +V) = -6.5$; and $\Pi_p(LA, -V) \approx -7.4$ in units of 10^{-11} cm²/dyn.

It is to be expected that Π_p of the direct tunneling current at very small biases is different from that of the indirect tunneling current. Furthermore, one expects the following relationships to hold between the magnitudes of Π_p : (i) $\Pi_p(LA, +V) < \Pi_p(TA, +V)$ and $\Pi_p(LA, -V) > \Pi_p(TA, -V)$, and (ii) $\Pi_p(LA, +V) < \Pi_p(LA, -V)$ and $\Pi_p(TA, +V) < \Pi_p(TA, -V)$. The reason for this is the change in β of Eq. (2) produced (i) by the difference in energy of the *TA* and *LA* phonons and (ii) by the reversal of the sign of $\hbar\omega$ as the bias is reversed.

The observed stress coefficients obey relation (ii). The differences in Π_p as observed upon reversal of bias agree with Eq. (2) to within the experimental accuracy. However, the relation (i) is not satisfied. The average $\frac{1}{2}[\Pi_p(LA, +V) + \Pi_p(LA, -V)]$, instead of being equal to the equivalent average of the Π_p in the *TA* phonon regions as predicted by Eq. (2), is about 25% larger in absolute magnitude. If this difference is interpreted as resulting from a difference in β in the two-phonon regions, then the tunneling probability would be a factor of 100 larger in the *TA* than in the *LA* phonon region. It is considered unreasonable that a difference in the electron-phonon coupling constants of the two phonons could compensate for such a large factor to give the same magnitude of the current densities in the two-phonon regions as is observed experimentally. The change of Π_p at the transition from the *TA* to the *LA* phonon region is, therefore, not understood at present.

The dip in Π_p observed at ± 6 mV is probably due to

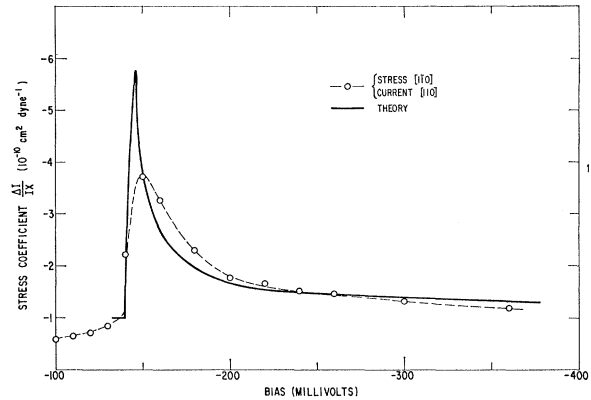


FIG. 6. Comparison between theoretical and experimental stress coefficient for reverse bias voltages beyond the Kane kink.

the change in the phonon energy with pressure. This dip is reproduced fairly well by a calculation based on the value of $d \ln(\hbar\omega)/dp = -12 \times 10^{-12}$ cm²/dyn for the *TA* phonon. The details of this calculation and the comparison with experiment will appear elsewhere.

The pressure coefficient of sample 1 in the indirect tunneling range is due to the change of the indirect band gap $E_g(111)$ and that of the reduced mass m^* . Neglecting the minor stress variations of C_i and D one can write from Eq. (2)

$$\frac{\Delta I_i}{I_i} = -\beta \left[\frac{3 \Delta E_g(111)}{2 E_g(111)} + \frac{1}{2} \frac{\Delta m^*}{m^*} - \frac{\Delta F}{F} \right]. \quad (13)$$

One may estimate β from Eq. (13) and the measured $\Pi_p = 6 \times 10^{-11}$ cm²/dyn of sample 1 in the forward bias range. Here again it is difficult to estimate $\Delta m^*/m^*$. The reduced mass m^* in Eq. (13) contains the light hole mass and the component of the (111) valley mass tensor in the field direction. The change of the light hole mass can be estimated from Eq. (12) where $[1/E_g(000)] \times [dE_g(000)/dp] = 12.4 \times 10^{-12}$ cm²/dyn. The change of the transverse electron mass, which predominantly determines the component of the electron mass in the field direction, is related to the band gap change at the zone face at [111] which is $(1/E_g)(dE_g/dp) = 3.4 \times 10^{-12}$ cm²/dyn.¹⁸ Hence, $(1/m^*)(dm^*/dp) = (8 \pm 5) \times 10^{-12}$ cm²/dyn may be a reasonable estimate. Using this value and the measured pressure coefficient one obtains $\beta = 16 \pm 3$ for $V = +60$ mV. The same calculation yields the value $\beta = 20 \pm 4$ for $V = -70$ mV. This increase of β with decreasing bias voltage disagrees strongly with Eqs. (2) and (3) which predict instead a slight decrease of β .¹⁹

One may think that this discrepancy is due to some simplifying assumptions on which the derivation of

¹⁸ R. Zallen, W. Paul, and J. Tauc, *Bull. Am. Phys. Soc.* **7**, 185 (1962).

¹⁹ This effect was also observed by M. I. Nathan and W. Paul, in *Proceedings of the International Conference Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 209.

Eqs. (2) and (3) is based, in particular, the assumptions of (i) a constant junction field, (ii) a parabolic shape of the energy bands in \mathbf{k} space, and (iii) an abrupt transition from n -type to p -type doping. Nathan,²⁰ however, has calculated the tunneling exponent β using the more realistic field of a graded junction and including nonparabolic effects. He finds that both, the variation of the field with position in the junction and a graded impurity distribution, cause β to decrease with decreasing bias voltage even faster than predicted by Eqs. (2) and (3) and that the nonparabolic effects do not influence the bias dependence of β appreciably. In addition to this, Nathan finds that for interpreting the current-voltage characteristic of germanium diodes at 297°K one requires β to decrease with decreasing voltage. In comparing the current-voltage characteristic of the direct tunneling process beyond the Kane kink with Eqs. (2) and (3) in Fig. 5, we also concluded that α decreases with decreasing bias.

In view of this evidence it is difficult to understand the increase of β with decreasing bias voltage as observed in the hydrostatic pressure experiments.

Since one is dealing with the same diode, one should be able to calculate β from the previously determined $\alpha=17.6$ at $V=-300$ mV. Using Eqs. (1), (2), and Kane's value $\lambda_i/\lambda_d=16/3\pi$, one obtains for our case $\beta/\alpha=1.5$, and hence, $\beta=26.5$ at $V=-300$ mV. This value of β compares well with $\beta=23.5\pm 5$ obtained by extrapolating the *observed* bias dependence of β to $V=-300$ mV. However, in view of the unexpected bias dependence of β , this agreement may be fortuitous.

The contribution to the stress coefficient of sample 2 which arises from the nonequivalence of the two pairs of valleys consists of two parts. (1) The shear causes some electrons to transfer from the two valleys which are raised in energy into the two which are lowered. Those which are lowered are the easy valleys, i.e., they have the smaller m^* in the tunneling direction. Hence we expect this part to give a positive contribution to Π . (2) The shift of the valleys will change also the tunneling probability because the energy gap for a particular valley is changed. Since the easy valleys are lowered in energy, their energy gap decreases under shear. This again results in a positive contribution to Π .

Since the first effect involves the density of states factor D , one has to write the current as a sum over the j valley contributions and the k -phonon contributions

$$I = \sum_{jk} I_{jk}, \quad (14)$$

where

$$I_{jk} = A_k D (eV \pm \hbar\omega_k/e) \exp(-\beta_j), \quad (15)$$

with

$$\beta_j = \lambda_i E_g^{3/2}(111) m_j^{*1/2} / F. \quad (16)$$

The plus and minus signs in Eq. (15) indicate that the phonon voltage $\hbar\omega_k/e$ has to be subtracted from the magnitudes of both the forward and the reverse bias

voltage for calculating D_k . The coefficients A_k take into account the different electron-phonon interaction strengths for the two phonons.¹² From Fig. 3 we determined $A_2/A_1=2.23$, where A_2 refers to the higher energy phonon.

The stress coefficient due to the nonequivalence of the valleys will, then, be

$$\Delta I / IX = \sum_{jk} \Delta I_{jk} / \sum_{jk} I_{jk} X. \quad (17)$$

From Eq. (15) one obtains

$$\Delta I_{jk} = A_k \exp(-\beta_j) \times \left[\frac{dD_k}{d(\zeta_n)} (\Delta\zeta_n)_j - \frac{3}{2} \frac{D_k \beta_j}{E_g(111)} \Delta E_{g_j}(111) \right]. \quad (18)$$

Equation (18) does not include the effect of shear on the transverse and longitudinal electron masses in the (111) valleys. This effect depends not only on the shifts of the conduction band valleys with shear but also on the equivalent quantities for the valence bands at the (111) zone face. These latter quantities are not accurately known at present. In any case, this effect would give rise to a contribution which is independent of bias similar to the second term in Eq. (18). It would, therefore, cause a change in the constant value which the theoretical curve approaches at large reverse bias, but it would not otherwise affect the bias dependence of the shear stress coefficient. Our conclusions would not be affected by the inclusion of this term.

Since we consider in (17) the pure shear part of the stress only we have

$$\sum_j (\Delta\zeta_n)_j = 0, \quad \sum_j \Delta E_{g_j}(111) = 0, \quad (19)$$

and hence

$$(\Delta\zeta_n)_j = -\Delta E_{g_j}(111). \quad (20)$$

For uniaxial compression along $[1\bar{1}0]$ one finds

$$\Delta E_{g_3}(111) = -\Delta E_{g_1}(111) = \frac{1}{6} E_2 S_{44} X. \quad (21)$$

Here the subscript 1 refers to the easy valleys $j=1,2$, and subscript 3 to the hard valleys $j=3,4$. $E_2=19$ eV is the deformation potential for pure shear²¹ and $S_{44}=1.47 \times 10^{-12}$ cm²/dyn is the elastic compliance constant.²²

In the second term of Eq. (18), which is due to the change in tunneling probability, we have neglected the shear-induced change of the valley masses. Since the reduced mass is determined more by the light hole mass than by the electron mass, this effect is not large. Any change in the light hole mass, however, will affect both samples in the same way and hence will not contribute to the difference of Π of the two samples.

Because of the uncertainties involved in the previous determinations of α and β , we have adjusted the value of β_1 so that the magnitude of Eq. (17) agrees with the dif-

²⁰ M. I. Nathan, J. Appl. Phys. **33**, 1460 (1962).

²¹ H. Fritzsche, Phys. Rev. **115**, 336 (1959).

²² M. E. Fine, J. Appl. Phys. **24**, 388 (1953).

ference in Π of the two samples in the region where only the first phonon contributes. With $\beta_1/\beta_3 = (m^*_1/m^*_3)^{1/2}$ we obtained $\beta_1=16$ and $\beta_3=18$, both values quoted for $V=0$.

Figure 7 shows the comparison of Eq. (17) with the difference in Π of the two samples. Although the structure of the bias dependence is reproduced quite well by the theoretical curve, the agreement is only qualitative. The effect of the shift in valley population can clearly be seen in the region between 0.008 and 0.030 V bias. The discrepancy becomes large, however, as soon as the higher energy phonon starts to contribute to the tunneling current. Here the experimental data fall off abruptly from the theoretical curve. There is no known reason why the two phonons should behave differently, but in order to see what would happen, a curve was plotted as though the valleys were equivalent for tunneling involving the higher energy phonons. This curve is shown dashed in Fig. 7. As can be seen from the forward bias data, this modification is too drastic. The data in the reverse bias direction are in better agreement, but it is hard to imagine any mechanism which would distinguish forward from reverse bias. The falloff of the data in the reverse bias direction will be affected by exactly the same smearing out mechanisms which are active beyond the Kane kink. If these mechanisms are indeed responsible for the slow falloff in that region, similar behavior in this bias region is to be expected also. This smearing would not, however, account for the fact that the observed difference between the Π of the two samples near $V=-0.13$ V is appreciably smaller than the calculated shear coefficient. We, therefore, conclude that the variation of the inherent tunneling probability per electron is not as sensitive to shear as would be expected. Within the framework of the theory the only possibilities which can account for this are: (a) that the chosen value for β is too low; (b) that the effect of shear on the reduced effective mass is quite large and in the opposite direction as the effect of the valley energy shifts.

There is no value of β which is simultaneously consistent with the shear data and the hydrostatic pressure data. In view of the general agreement between the various independent calculations of β , possibility (a) is unlikely. Possibility (b) can be eliminated also because of the similarity of Π for sample 1 and Π_p . Furthermore, the mechanism responsible for the discrepancy beyond 30 mV in the forward bias region is undoubtedly also operating in this bias region. It, therefore, seems that a different mechanism not accounted for by the present theory contributes to the shear stress coefficient.

C. Comparison of Absolute Magnitudes of Tunneling Parameters with Theory

The physical properties of a diode determine the stress coefficient through the parameters α and β . These parameters could not be determined unambiguously

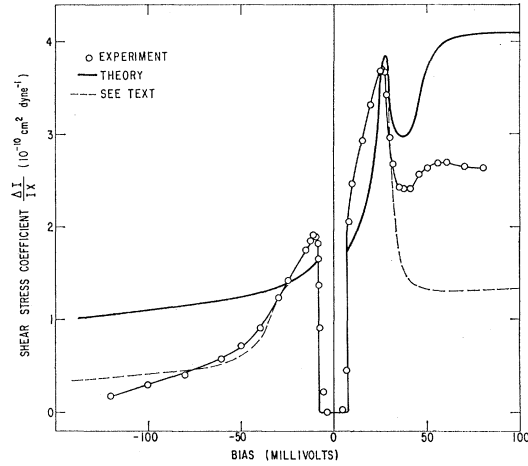


FIG. 7. The difference between the uniaxial stress coefficients of samples 1 and 2. Comparison between theory and experiment. The heavy curve represents the theory based on the anisotropy of the tunneling probability in the whole bias range of indirect tunneling. The dotted curve was calculated assuming that the (111) valleys are equivalent for tunneling involving the higher energy phonon.

from the stress coefficients because the stress-induced changes of the relevant effective masses are not known. These measurements would yield these effective mass changes if it were possible to determine the parameters α and β by some other method. The theory leading to Eqs. (1) and (2) does not determine these parameters accurately enough since it is based on the assumption of a constant junction field and neglects the spatial distribution and fluctuations of the impurity concentrations near the junction.

It is, nevertheless, interesting to compare and evaluate the values of α and β predicted by the constant junction field theory with the values obtained above from the stress coefficients using reasonable estimates for $\Delta m^*/m^*$. The coefficients α and β can be obtained from the theory, (i) by direct computation using Eqs. (1), (2), and (3), and (ii) by calculating C and D and using the measured I for a given bias voltage. This was done with the following choice of parameters appropriate for our diodes: $\zeta_p=0.15$ eV, $\zeta_n=0.020$ eV, $p=6 \times 10^{19}$, $n=5.5 \times 10^{18}$, junction area = 0.002 cm², $\kappa=16$, $I_d=0.370$ A at $V=-300$ mV.

The values for α and β obtained by method (i) are listed in the first row of Table I. The third row gives α

TABLE I. Values of tunneling exponents α and β .

	α	Bias (mV)	β	Bias (mV)
Theory	8.5	-300	12.5	-300
Theory (see text)	12	-300	17.5	-300
Theory and I_d	12.5 ± 1	-300		
Pressure exp.	17.6	-300	16 ± 3	+60
Pressure exp.			20 ± 4	-70
Shear exp.			17 ± 1	0

as calculated by method (ii). The value of β could not be obtained in this way because the electron-phonon coupling constants are not known. The fourth and fifth rows list the values obtained from the experimentally observed hydrostatic pressure coefficients as explained in the previous section. The last row gives the value of β used to fit the shear contribution to the stress coefficient of sample 2 in the bias range of indirect tunneling. The bias voltages at which the listed quantities were obtained are included in Table I.

It is seen that α and β as computed from the constant field expressions Eqs. (1), (2), and (3) are appreciably smaller than the other values. This is to be expected since a real diode will have a more diffused distribution of impurities, and hence, a smaller impurity concentration near the junction than in the bulk material. This yields a wider junction. Following Meyerhofer *et al.*,²³ we assume the donor concentration near the junction to be half of that of the bulk and obtain by direct computation of α and β the values quoted in the second row of Table I.²⁴

The uncertainty of the experimental values stems from the difficulty of estimating $\Delta m^*/m^*$ and also from the fact that for the pressure coefficients of the energy gaps the values measured on pure material at 300°K were used. It is hoped to obtain the temperature dependence of these pressure coefficients by studying the stress tunneling coefficients at elevated temperatures.

V. SUMMARY AND CONCLUSION

The magnitude and the orientation dependence of the effect of stress on the tunneling current enables one to distinguish three different tunneling processes in Sb-doped germanium.

(1) In the small bias range $-8 \text{ mV} < V < +8 \text{ mV}$ the tunneling is direct. The detailed nature of the tunneling process in this range is not known. The current is not affected by the relative shifts of the (111) valleys under shear and hence cannot arise from a sum of independent (111) valley contributions.

(2) Beyond about 8 mV at helium temperatures, but before the onset of direct tunneling into the (000)

conduction band, the tunneling process is phonon assisted. Here a large additional contribution to the stress coefficient is observed for a shear stress which lifts the degeneracy of the (111) valleys when the orientation of the junction field is such that the effective mass components of the valleys in the field direction are different. This demonstrates clearly the anisotropy of the tunneling probability when the effective mass is anisotropic as predicted by the theory.

(3) For biases $V < -140 \text{ mV}$, direct tunneling into the (000) conduction band is observed. Near the onset voltage V_k the magnitude of the stress coefficients increases sharply because of the pressure dependence of V_k . This sharp increase allows an accurate determination of $E_g(000) - E_g(111)$, the energy separation between the conduction band edges at (000) and (111), respectively. We find for this the value $0.160 \pm 0.005 \text{ eV}$ which is about 0.015 eV larger than that for pure material. This larger value of the conduction band separation agrees with recent results of infrared absorption measurements¹⁶ in degenerate germanium. The sharp rise of the stress coefficients near $V = V_k$ indicates that the (000) conduction band edge is quite well defined despite the large impurity concentration.

The major features of the bias and orientation dependencies of the stress coefficients agree with the present theory of tunneling. There are, however, several interesting observations which remain unexplained at present. One is the structure in the bias dependence of the pressure coefficient Π_p . The apparent value of the tunneling exponent β is approximately 25% larger in the *LA* phonon region than in the *TA* phonon region. The second is the disagreement between the theoretically predicted shear contribution to Π with the experiments in the bias range where *LA* phonons can be emitted. Apparently the way in which the phonons are incorporated into the theory does not adequately describe their differences. The third observation which needs some further study is the bias dependence of the indirect tunneling exponent β which is found to be opposite to the prediction of theory.

ACKNOWLEDGMENTS

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²³ D. Meyerhofer, G. A. Brown, and H. S. Sommers, Phys. Rev. **126**, 1329 (1962).

²⁴ Nathan discussed and employed a method for obtaining β from the bias dependence of the reverse current at room temperature (see reference 20). Although several aspects of the shape of the *I-V* characteristic still remain unexplained we have used his method and find for our samples at zero bias $\beta = 18 \pm 1$ using his best-fit parameter $\gamma = 1.25$.