order to explain these results with the concepts used in those models.

Mycielski[21] suggests that the conduction in question may be due to hopping over instead of tunneling through the Coulomb potential wall separating neighboring donors. This differs from previous models only in the way the effective height of the potential wall is calculated. The expression derived by Mycielski does not predict a stress dependence of ϵ_2 for a donor like Sb which has a very small valley-orbit splitting.

V. CONCLUSIONS

Germanium offers a unique opportunity to study the effect of the correction to the effective-mass approximations on the donor levels and on their wave functions because it has donors with greatly different valley-orbit splitting energies. For Sb the effective mass approximation is nearly correct, whereas As shows a valley-orbit splitting which is almost one-half of the effective-mass binding energy.

It is surprising that the differences in the impurity cell correction are distinctly observable even at the transition to metallic conduction where the interaction between impurities is very strong. It is interesting to investigate whether these differences affect the metallic conduction properties at even higher impurity concentrations. Preliminary experiments of the low temperature piezoresistance effect at concentrations larger than 4×10^{17} cm^{-3} show no difference between Sb- and As-doped germanium. The characteristics of Esaki diodes, however, show a difference between the donor elements.[22]

Several advantages of the use of shear strains for the investigation of impurity conduction have been mentioned and illustrated in this paper. The results obtained at large [111] compression may be better suited for a theoretical interpretation than those obtained at zero stress because of the simple, almost hydrogen-like donor level scheme produced by the compressional stress. Investigations are presently in progress of the anisotropy of the piezoresistance in the low and intermediate concentration ranges. They seem to yield further information about the nature of the observed activation energies.

The conclusions which can be drawn from the reported data concerning the strain-induced changes of the donor wave functions will be discussed in the following paper (II).

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[22] N. Holonyak, I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, Phys. Rev. Letters **3**, 167 (1959).

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Effect of Stress on the Donor Wave Functions in Germanium*

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The effect of the corrections to the effective-mass approximation on the stress dependence of the donor wave functions has been re-examined. It is found that not only the relative valley contributions to the ground-state wave function are changed by the stress, but also the individual envelope functions $F_j(\mathbf{r})$ which originate from the j conduction-band valleys. The stress dependence of the $F_j(\mathbf{r})$ depends strongly on the value of the valley-orbit splitting of the donor. This can explain qualitatively the different behavior of the piezoresistance effect in the impurity conduction range of germanium doped with antimony, arsenic, or phosphorus. The stress dependence of the hyperfine splitting of the electron spin resonance is shown to be very insensitive to the stress-induced changes in $F_j(\mathbf{r})$ except in the limit of very large stresses.

I. INTRODUCTION

In previous calculations[1,2] of the strain-induced changes of the donor wave functions in germanium and silicon it was assumed that the only effect of strain is to admix to the ground state some of the higher-lying 1s-like states. As an example, consider the wave functions for the donor states in germanium which can be written according to Kohn and Luttinger[3] as

$$\Psi(\mathbf{r})=\sum_{j=1}^{4}\alpha_j F_j(\mathbf{r})\varphi_j(\mathbf{r}), \tag{1}$$

where φ_j is the Bloch function at the jth conduction band minimum and $F_j(\mathbf{r})$ is the effective-mass envelope

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

[1] H. Fritzsche, Phys. Rev. **119**, 1899 (1960). An error in this paper should be pointed out. The second line of Eq. (1) should read

$$\Psi^{(2)}=\tfrac{1}{2}\sum_{j=1}^{2}\left[1+\epsilon_j/(4\Delta_c^2+\epsilon_j^2)^{\frac{1}{2}}\right]^{\frac{1}{2}}\Phi_j-\tfrac{1}{2}\sum_{j=3}^{4}\left[1+\epsilon_j/(4\Delta_c^2+\epsilon_j^2)^{\frac{1}{2}}\right]^{\frac{1}{2}}\Phi_j.$$

[2] D. K. Wilson and G. Feher, Phys. Rev. **124**, 1068 (1961). G. Feher, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 579.

[3] For a review on this subject see: W. Kohn in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

function. The assumption that only the relative valley contributions to $\Psi(\mathbf{r})$ are affected by the stress implies that stress changes only the numerical coefficients α_j. These coefficients then depend on the stress X and on the valley-orbit splitting parameter Δ through the ratio X/Δ. The properties which depend on the donor wave functions should, therefore, be reducible for the various donor elements on a plot against X/Δ. This was indeed found to be the case for the strain-induced change of the hyperfine splitting of the electron spin resonance in silicon and in germanium.[2] Hence it was possible to determine from the stress dependence of the hyperfine splitting, the valley-orbit splitting energies of the various donors.[4]

In a previous paper,[5] hereafter referred to as I, we describe measurements of the effect of uniaxial [111] compression on impurity conduction in germanium. In contrast to the hyperfine splitting, which is proportional to the amplitude square of the donor wave function at the donor nucleus, impurity conduction depends on the amplitude of the donor wave function at large distances from the impurity. According to the previous treatments of the stress dependence of the donor wave function, which assumed a change only of the α_j, we expected the piezoresistance of impurity conduction to be approximately the same function of X/Δ for the different donor elements. We found this not to be the case.

Depending on whether antimony, arsenic, or phosphorus was used as donor, we observed great qualitative differences in the behavior of the piezoresistance of impurity conduction in the intermediate concentration range and in the stress dependence of the transition from nonmetallic to metallic conduction.

The largest effect of stress was found to be a change of the activation energy ϵ_2 of impurity conduction.[6] For Sb donors ϵ_2 increases strongly with [111] compression; for As and P donors, however, ϵ_2 decreases, the effect being larger for As than for P donors. We observed that the critical impurity separation d_c at which the transition[7] to metallic conduction occurs depends on the donor element and on stress. Compression along [111] decreases d_c for Sb donors. It increases d_c for As donors and to a smaller extent for P donors. At all stress values d_c remains largest for Sb and smallest for As donors.

This large difference in the behavior of the donor elements must be related to the corrections to the effective-mass approximation which give rise to the valley-orbit splitting of the 1s donor multiplet.[3,8] The valley-orbit splitting differs greatly for the different donors. It is $4\Delta=0.57\times10^{-3}$ ev for Sb,[9] $4\Delta=2.9\times10^{-3}$ ev for P,[10] and $4\Delta=4.15\times10^{-3}$ ev for As.[10,11]

In order to arrive at a qualitative understanding of the results of the piezoresistance measurements, which are discussed in greater detail in I, we want to reexamine in this paper the effect of the corrections to the effective-mass approximation on the stress dependence of the donor wave functions. Kohn and Luttinger mentioned already[3] that the correction potential which lowers the ground-state energy below the value obtained from the effective mass theory causes a reduction of the effective Bohr radius. This means the envelope functions $F_j(\mathbf{r})$ of the donor ground state at zero stress are changed by the correction potential.

In Sec. II of this paper we estimate the changes of the donor wave functions in germanium as a function of uniaxial compression along [111]. In Sec. III an attempt will be made to explain qualitatively the experimental results reported in I. In the last section we discuss the effect of strain on the hyperfine splitting of the electron spin resonance using the corrected envelope functions. The corrections to the effective-mass treatment will be discussed by W. D. Twose in the Appendix.

II. CALCULATION OF THE DONOR WAVE FUNCTIONS

A. Without Strain

The Kohn-Luttinger theory[3] of shallow donors yields Eq. (1) for the donor wave functions of germanium in the effective mass approximation. Each of the envelope functions $F_j(\mathbf{r})$ of the 1s-like donor states has the form of a pancake with its symmetry axis along that of the jth valley and can be written as follows:

$$F_j(\mathbf{r})=(\pi a^2 b)^{-\frac{1}{2}}\exp\{-[(x_j^2+y_j^2)/a^2+z_j^2/b^2]^{\frac{1}{2}}\}. \quad (2)$$

The parameters $a=64.5$ A and $b=22.7$ A for germanium were found by a variation calculation to yield the lowest energy. The direction of z_j lies along the [111] direction of the jth valley.

In the effective-mass approximation the ground state is fourfold degenerate. Symmetry arguments allow this state to split into a onefold and a threefold state. This splitting is caused by corrections to the effective-mass approximation, which in turn are due to a number of factors. Some of these are the finite charge of the impurity ion, the breakdown of the concept of the dielectric constant near the impurity, and the incomplete shielding of the donor nucleus inside the donor ion. All these factors have in common that they are appreciable only in the immediate vicinity of the donor atom. These deviations from the effective-mass approximation will be expressed by a correction potential $U(r)$ which is large only in or near the impurity cell.

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[4] Actually these measurements determine only the ratios of the shear deformation potential to the valley-orbit splitting energies.

[5] H. Fritzsche, preceding paper [Phys. Rev. **125**, 1552 (1962)].

[6] This activation energy determines the temperature dependence of impurity conduction in the intermediate impurity concentration range. For more details see reference 5.

[7] N. F. Mott, Can. J. Phys. **34**, 1356 (1956); N. F. Mott and W. D. Twose, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107.

[8] P. J. Price, Phys. Rev. **104**, 1223 (1956).

[9] H. Fritzsche, Phys. Rev. **120**, 1120 (1960).

[10] D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. **5**, 60 (1960); G. Weinreich and H. G. White, *ibid.* **5**, 50 (1960).

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

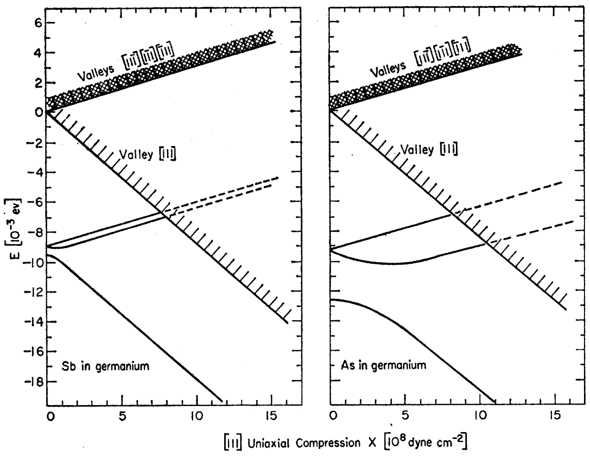

FIG. 1. Variations of the conduction band valleys and of the 1*s* donor levels, for Sb and As in germanium, caused by a uniaxial compression in the [111] direction.

Inclusion of the correction potential $U(r)$ leads to the following equation[12] for the $F_j(\mathbf{r})$ in the absence of strain:

$$\sum_{j=1}^{4} \alpha_j^{(i)} e^{i(\mathbf{k}_j-\mathbf{k}_l)\cdot\mathbf{r}} [H_j - E] F_j^{(i)}(\mathbf{r}) + \sum_{j=1}^{4} \alpha_j^{(i)} e^{i(\mathbf{k}_j-\mathbf{k}_l)\cdot\mathbf{r}} U(r) F_j^{(i)}(\mathbf{r}) = 0. \quad (3)$$

H_j is the effective-mass Hamiltonian appropriate to the jth valley and $\mathbf{k}_j$ is the wave vector to that valley. The superscript (i) runs from 1 to 4 labeling the different 1*s*-like donor states. Because of the short range of $U(r)$, the diagonal matrix elements of $U(r)$ are nearly equal to the off-diagonal matrix elements. Following Price, we set them equal to $-\Delta$. The solution of the secular equation yields the 1*s* multiplet.

$$\begin{aligned} E^{(1)} &= -E_{d0} - 4\Delta, \\ E^{(2)} = E^{(3)} = E^{(4)} &= -E_{d0}, \end{aligned} \quad (4)$$

where $-E_{d0}$ is the lowest energy eigenstate of the effective-mass Hamiltonian H_j. The completely symmetric state $\alpha^{(1)} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ having a large amplitude in the impurity cell is the only one affected by the short-range potential $U(r)$. The energy difference 4Δ, called the "chemical shift" or "valley-orbit splitting," depends on the donor element.

Since $E^{(1)}$ lies below the effective-mass value E_{d0}, the ground state wave function $\Psi^{(1)}$ will be more concentrated near the impurity ion than $\Psi^{(2)}$, $\Psi^{(3)}$, and $\Psi^{(4)}$ of the three upper states. Thus $F_j^{(i)}(\mathbf{r})$ depends on the ith donor state. Following Kohn and Luttinger we estimate the asymptotic behavior of $F_j^{(1)}(r)$ at large r, where $U(r) = 0$, from

$$[H_j - E^{(1)}] F_j^{(1)}(\mathbf{r}) = 0, \quad (r = \text{large}). \quad (5)$$

Each of the envelope functions $F_j^{(1)}(\mathbf{r})$ of the ground state falls off exponentially with an effective Bohr radius:

$$a^{(1)} = a(\text{eff. mass})(E_{d0}/E_{d0} + 4\Delta)^{\frac{1}{2}}. \quad (6)$$

If the anisotropy of the $F_j^{(1)}$ is not changed by the correction potential, then both parameters a and b of Eq. (2) will be reduced according to Eq. (6).

For the higher lying threefold state, the terms in Eq. (3) containing $U(r)$ will sum approximately to zero and $a^{(2)} = a^{(3)} = a^{(4)} = a(\text{eff mass})$. The splitting parameter Δ is then more accurately given by the matrix elements of $U(r)$ using the corrected envelope functions $F_j^{(1)}(\mathbf{r})$.

B. With Strain

When the crystal is subjected to shear, the degeneracy of the conduction band valleys is in general destroyed. The shift of the valleys ϵ_j due to the shear component of compression along [111] is given by the deformation potential theory[13] as

$$\begin{aligned} \epsilon_1 &= -3\epsilon, \\ \epsilon_2 = \epsilon_3 = \epsilon_4 &= \epsilon, \end{aligned}$$

with

$$\epsilon = \tfrac{1}{9} E_2 S_{44} X. \quad (7)$$

$S_{44} = 1.47 \times 10^{-12}$ cm²/d is the elastic shear constant[14] and $E_2 = 19$ ev/strain is the deformation potential for pure shear.[11] The stress X, parallel to [111], is positive for compression. The valleys are labeled from $j=1$ to $j=4$ according to the direction of their axes along [111], [$11\bar{1}$], [$1\bar{1}1$], and [$1\bar{1}\bar{1}$], respectively.

Including the shifts of the valleys in Eq. (3) and assuming that $U(r)$ is unaffected by the strain, we obtain[12]

$$\sum_{j=1}^{4} \alpha_j^{(i)} e^{i(\mathbf{k}_j-\mathbf{k}_l)\cdot\mathbf{r}} (H_j + \epsilon_j - E^{(i)}) F_j^{(i)}(\mathbf{r}) + \sum_{j=1}^{4} \alpha_j^{(i)} e^{i(\mathbf{k}_j-\mathbf{k}_l)\cdot\mathbf{r}} U(r) F_j^{(i)}(\mathbf{r}) = 0. \quad (8)$$

In the following we try to obtain an approximate solution for the asymptotic form of $\Psi^{(i)}$ at large r as a function of stress. First we assume $F_j^{(i)}$ to be the same for all (i) and equal to the solution of the effective mass Hamiltonian H_j. Price[8] solved the resulting secular equation and obtained[15] the donor states:

$$\begin{aligned} E^{(1)} &= -E_{d0} - \epsilon - 2\Delta - 2(\Delta^2 - \Delta\epsilon + \epsilon^2)^{\frac{1}{2}}, \\ E^{(2)} = E^{(3)} &= -E_{d0} + \epsilon, \\ E^{(4)} &= -E_{d0} - \epsilon - 2\Delta + 2(\Delta^2 - \Delta\epsilon + \epsilon^2)^{\frac{1}{2}}. \end{aligned} \quad (9)$$

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[12] See Appendix.

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

[14] M. E. Fine, J. Appl. Phys. **24**, 338 (1953).

[15] Our result differs from his only in that we assumed the diagonal and the off-diagonal matrix elements of $U(r)$ to be equal. This leaves at zero stress the higher lying threefold state unaffected by the correction potential.

Figure 1 shows for [111] compression the donor level scheme of Sb and of As in germanium. We set $x=\epsilon/\Delta$ and $\Phi_j^{(i)}=\varphi_j F_j^{(i)}$, solve for the coefficients $\alpha_j^{(i)}$, and obtain the corresponding wave functions:

$$\begin{aligned}
\Psi^{(1)}(x)&=\frac{1}{\sqrt{2}}\left[1+\frac{2x-1}{2(x^2-x+1)^{\frac12}}\right]^{\frac12}\Phi_1^{(1)}\\
&\quad+\frac{1}{\sqrt{6}}\left[1-\frac{2x-1}{2(x^2-x+1)^{\frac12}}\right]^{\frac12}(\Phi_2^{(1)}+\Phi_3^{(1)}+\Phi_4^{(1)}),\\
\Psi^{(2)}(x)&=\frac{1}{\sqrt{2}}(\Phi_2^{(2)}-\Phi_3^{(2)}),\\
\Psi^{(3)}(x)&\frac{1}{\sqrt{6}}(\Phi_2^{(3)}+\Phi_3^{(3)}-2\Phi_4^{(3)}),\\
\Psi^{(4)}(x)&=\frac{1}{\sqrt{2}}\left[1-\frac{2x-1}{2(x^2-x+1)^{\frac12}}\right]^{\frac12}\Phi_1^{(4)}\\
&\quad+\frac{1}{\sqrt{6}}\left[1+\frac{2x-1}{2(x^2-x+1)^{\frac12}}\right]^{\frac12}(\Phi_2^{(4)}+\Phi_3^{(4)}+\Phi_4^{(4)}).
\end{aligned}\tag{10}$$

So far we have assumed $\Phi_j^{(i)}$ to be the same for all donor states (i). Now we estimate the asymptotic form of $F_j^{(i)}(\mathbf{r})$ at large r in a way similar to the zero stress case. At large r the terms in Eq. (8) containing $U(r)$ can be neglected because of the short range of the correction potential, so that the asymptotic form of $F_j^{(i)}(\mathbf{r})$ is determined by

$$[H_j+\epsilon_j(x)-E^{(i)}(x)]F_j^{(i)}(\mathbf{r},x)=0. \tag{11}$$

The effective Bohr radius depends on both the donor state number (i) and the valley number j. It is approximately given by

$$a_j^{(i)}(x)=a(\text{eff. mass})\{-E_{d0}/[E^{(i)}(x)-\epsilon_j(x)]\}^{\frac12}. \tag{12}$$

In the special case of uniaxial stress along [111], $E^{(i)}(x)$ is given by Eq. (9) and $\epsilon_j(x)$ by Eq. (7). According to Eq. (12) the effective Bohr radius of the jth envelope function of the ith donor state depends on the ratio of the effective-mass binding energy E_{d0} to the energy difference between the ith state and the jth conduction band edge. Figure 2 shows the ratios $a_j^{(1)}/a$ of the ground state as a function of compressional [111] stress for the various donor impurities in germanium. At zero stress, the ground-state orbit of As is about 17% smaller than its effective-mass value because of the large valley-orbit splitting 4Δ. The orbit of $\Phi_1^{(1)}$ expands with increasing compression up to a certain limiting value which is still smaller than that of the effective-mass theory. This expansion of the orbit is of course most pronounced in the case of As donors which have the smallest orbit at zero stress. The radii of $\Phi_2^{(1)}$, $\Phi_3^{(1)}$, and $\Phi_4^{(1)}$ shrink considerably for all donor elements. It is interesting to note that the orbit radius of $\Phi_1^{(1)}$, which is the limiting form of $\Psi^{(1)}$ at large compressional stresses, becomes in the high stress limit almost the same for Sb, As, and P. It differs only by a few percent from the effective-mass value. The question whether the anisotropy of the envelope functions, that is the ratio a/b, remains unaffected by the stress is still unresolved.

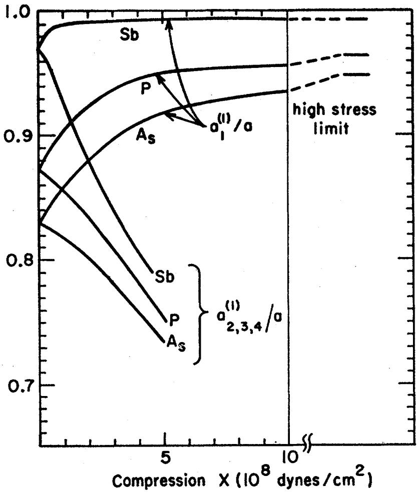

FIG. 2. The ratios $a_j^{(1)}/a$ of the ground state as a function of compressional [111] stress for the various donor elements in germanium. See Eq. (12) of text.

The error made in using the uncorrected $F_j(\mathbf{r})$ for the calculation of $\alpha_j^{(i)}(x)$ and $E^{(i)}(x)$ is probably not large. It comes primarily from the fact that with $F_j^{(i)}(\mathbf{r},x)$ also the matrix elements of $U(r)$ become stress dependent. How the stress dependence of $F_j^{(1)}(\mathbf{r},x)$ changes the ground state energy $E^{(1)}(x)$ can be estimated in the high-stress limit. There one deals with a one-valley semiconductor and $\Psi^{(1)}(\mathbf{r},\infty)=\varphi_1(\mathbf{r})F_1^{(1)}(\mathbf{r},\infty)$. The correct $F_1^{(1)}(\mathbf{r},\infty)$ is less concentrated around the impurity ion than any of the $F_j^{(1)}(\mathbf{r},0)$, which determine Δ at zero stress. Hence the amplitude of $F_1^{(1)}(\mathbf{r},x)$ at $r=0$ and consequently the matrix element

$$\Delta=(F_1^{(1)}|U(r)|F_1^{(1)})$$

is reduced by the stress. Thus Δ, the depression of $E^{(1)}(\infty)$ below its effective-mass value $-E_{d0}$ is less than one quarter of the valley-orbit splitting at zero stress. This fact brings $a_1^{(1)}(\infty)$ of the various donor elements even closer to the value of a(eff. mass).

III. COMPARISON WITH EXPERIMENTAL RESULTS

In this section we wish to evaluate the effects of uniaxial [111] compression on impurity conduction, which have been reported in I, in terms of the stress dependence of the donor wave functions calculated in the previous section. The main features of the experimental results can be seen in Fig. 13 of I. They are the following:

(1) In the absence of strain the critical impurity separation d_c of the transition to metallic conduction is very different for the various donor elements. It is largest for Sb and smallest for As.

(2) In the limit of large [111] compression the donor elements behave almost alike. However, Sb still seems to have a slightly larger effective Bohr radius than As.

(3) Compression along [111] decreases the effective overlap of neighboring impurity states for Sb donors, it increases the overlap for As and to a smaller extent also for P donors.

The first feature agrees with the theoretical predictions since according to Eq. (6) the ground state wave function at zero stress is more concentrated around the donor ion the larger its valley-orbit splitting is. This is shown in Fig. 2 where at zero stress the Bohr radius becomes progressively smaller as one goes from Sb to P and to As. As a consequence one needs in the case of P and As a larger impurity concentration than in the case of Sb to obtain a given value of the activation energy ϵ_2 or to reach the transition to metallic conduction.

The second feature indicates that the Bohr radii of the different donor elements become nearly the same at large compressional stresses along [111] where $\Psi^{(1)}(\mathbf{r}) = \Phi_1^{(1)}(r,\infty)$. This agrees with Eqs. (10) and (12). Figure 2 shows that the values of $a_1^{(1)}/a$ differ greatly at zero stress and that they become almost identical at large stresses. The small differences in Bohr radii still remaining in the high-stress limit are also observable experimentally.

In order to understand the third feature, that is the decrease in overlap in the case of Sb and the increase in overlap in the case of As donors as [111] compression is applied, one has to consider the two opposing effects which change the donor wave functions.

The first effect is present in both cases of large and of small valley-orbit splittings. It results in a decrease in the average overlap of the ground state wave functions of neighboring donors and is due to the following. The [111] compressional stress reduces the contributions to $\Psi^{(1)}(\mathbf{r})$ of the three valleys 2, 3, and 4 which move up in energy [see Eq. (10)]. Consequently the coefficients $\alpha_{234}^{(1)}(x)$ decrease until they vanish in the high stress limit. At the same time the orbit radii of $\Phi_2^{(1)}$, $\Phi_3^{(1)}$, and $\Phi_4^{(1)}$ shrink as shown in Fig. 2 and thereby increase the rate at which the overlap reduces with increasing stress.

The second effect is the expansion of the Bohr radius of the valley function $\Phi_1^{(1)}(\mathbf{r})$. It can increase the overlap, particularly in the case of donors which have a large valley-orbit splitting and hence a very compact ground-state wave function at zero stress. Figure 2 shows the growth of $a_1^{(1)}/a$ with increasing compression for the three donor elements.

For Sb donors this second effect is negligible. We therefore expect a decrease of the average overlap due to the change of the valley contributions. This agrees with the experimental observations.

TABLE I. Ratios of the effective Bohr radii.

	Large stress		Zero stress	
	$a_{HX}(\mathrm{Sb})/a_{HX}(\mathrm{As})$	$a_{HX}(\mathrm{P})/a_{HX}(\mathrm{As})$	$a_{H0}(\mathrm{Sb})/a_{H0}(\mathrm{As})$	$a_{H0}(\mathrm{P})/a_{H0}(\mathrm{As})$
Experiment	1.10±0.02	1.06±0.02	1.56±0.03	1.08±0.03
Theory	1.05	1.02	1.17	1.054

In the case of As and P donors both changes of the wave functions are effective and one cannot tell in advance which of the two is more important unless one knows which angular average of the overlap enters into the expression of the activation energy ϵ_2. The experimental results indicate, however, that the expansion of $\Phi_1^{(1)}(\mathbf{r})$ predominates in the case of As donors giving rise to an increase in overlap with increasing compression. For P donors the two opposing effects seem almost to compensate one another so that only a much smaller increase in overlap results.

In Table I we compare the theoretical values for the ratios of the Bohr radii of the different donor elements obtained from Eq. (12) with the experimental values listed in Table II of I. Although the theoretical and experimental values show the same trend, the quantitative agreement is not good. This, however, is not surprising in view of the fact that we do not know how and what angular average of the overlap determines the activation energy ϵ_2 and the transition to metallic conduction. Some other reasons for the discrepancy may be: (1) The fact that saturation of the piezoresistance effect had not yet been reached for the P- and As-doped samples, (2) that the ratio a/b of Eq. (2) might depend on the valley-orbit splitting and on the stress, hence the angular average of the overlap might yield a slightly different result for the different donors, and (3) the fact that we neglected at zero stress the effect on ϵ_2 of the higher lying threefold state, the wave functions of which are believed to be nearly the same for the various donor elements. Furthermore, in the previous section we treated the effect of stress on the wave functions of *isolated* donors. Changes of the wave functions due to the interaction of neighboring impurities have not been considered. These may play an important role at the high impurity concentrations of the samples used for the experiments. That the experimental results show the characteristics of the isolated donor wave functions at all may be due partly to the fact that the conductivity is predominantly limited by regions in the crystal where the average impurity separation is larger than the statistical average.

In calculating from Eq. (12) the ratios of the Bohr radii listed in Table I we used $E_{d0} = 9.2 \times 10^{-3}$ ev, the effective mass ionization energy of the isolated donor. It is known,[16] however, that the ionization energy decreases with increasing impurity concentration. A

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[16] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949); P. P. Debye and E. M. Conwell, *ibid.* **93**, 693 (1954).

smaller value of E_{d0} would bring the theoretical values in Table I into closer agreement with the experimental values.

According to Mott and Twose[7] the transition to metallic conduction occurs at a critical separation $d_c = \lambda a_H$. Using a_H(eff. mass) = 45 A as an appropriate angular average of the Bohr radius in the effective-mass approximation and scaling the Bohr radii according to Eq. (12), we obtain the following values for λ from the experimentally determined d_c. At zero stress $\lambda(\mathrm{Sb}) = 3.15$, $\lambda(\mathrm{As}) = 2.36$, $\lambda(\mathrm{P}) = 2.42$ and at maximum stress $\lambda(\mathrm{Sb}) = 2.3$, $\lambda(\mathrm{As}) = 2.14$, $\lambda(\mathrm{P}) = 2.19$. These values are to be compared with $\lambda = 3.7$ of Mott and Twose.[17]

The experimental values are considerably lower than the theoretical value. As far as the accuracy and the interpretation of the experimental results are concerned the same arguments apply to this case as those discussed above in connection with the discrepancy of the values listed in Table I.

IV. EFFECT OF STRESS ON $|\Psi^{(1)}(0)|^2$

Wilson and Feher[2,10] were able to explain their results on the stress dependence of the hyperfine splitting of the electron spin resonance in germanium and silicon without taking into account the changes of the individual valley wave functions $\Phi_j^{(i)}(\mathbf{r})$. Both the theory and the piezoresistance experiments show, however, that these wave functions change considerably with stress due to the corrections to the effective mass approximation. In the following we try to estimate by how much the stress dependence of $|\Psi^{(1)}(0)|^2$ is affected if one considers not only the changes with [111] compression of the coefficients $\alpha_j^{(1)}(x)$ but also of the functions $\Phi_j^{(1)}(0)$.

First we calculate the relative change of the hyperfine splitting under [111] stress in the approximation of Wilson and Feher. Assuming $\Phi_j^{(1)}(0)$ to be constant we can set $\Phi_j^{(1)}(0) = \Phi_0(0)$ and obtain with Eq. (10)

$$|\Psi^{(1)}(0,x)|^2/4|\Phi_0(0)|^2 = \tfrac{1}{2}[1+(2-x)/2(x^2-x+1)^{\frac{1}{2}}]. \quad (13)$$

The curve in Fig. 3 shows the result of Eq. (13). In Sec. II we obtained an asymptotic solution of Eq. (8) for large distances from the donor ion. We can make only a very rough estimate of the stress-induced changes of $\Phi_j^{(1)}(0)$. We assume: (1) that the amplitudes of the envelope functions $F_j^{(1)}(\mathbf{r})$ at $r=0$ change with $a_j^{(1)}(x)$ like the hydrogen-like functions of Eq. (2), and (2) that the ratio a/b remains constant. One obtains then

$$F_j^{(1)}(0,x)/F_j^{(1)}(0,0) = [a_j^{(1)}(0)/a_j^{(1)}(x)]^{\frac{3}{2}}, \quad (14)$$

with $a_j^{(1)}(x)$ given by Eq. (12). These assumptions are very crude but we believe that the results of this calculation remain almost unchanged even if Eq. (14) is replaced by a more exact expression. Including both, the stress dependence of the coefficients $\alpha_j^{(1)}(x)$ and that of the valley wave functions $\Phi_j^{(1)}(0)$, we obtain for the relative change of the hyperfine splitting of As donors the values represented by the points in Fig. 3. Up to $x=3$ the two calculations agree almost exactly although the wave functions change considerably. The decrease of $\Phi_1^{(1)}(0)$ with increasing stress seems to be just compensated by the increase of $\Phi_{234}^{(1)}(0)$. A further reduction of the hyperfine splitting due to the decrease of $\Phi_1^{(1)}(0)$ is observable only at very large stresses, where the contribution of the three upper valleys to the ground-state wave function becomes very small.

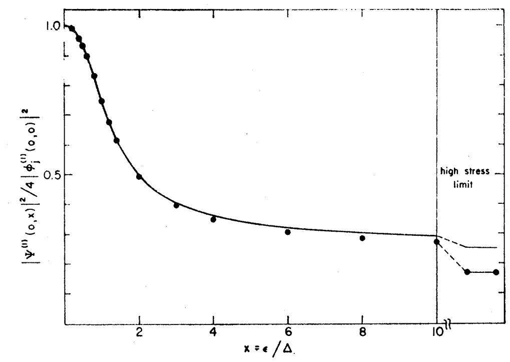

FIG. 3. Relative change of the hyperfine splitting under [111] compression in n-type germanium. The curve was calculated from Eq. (13) based on the approximation of Wilson and Feher. The points calculated for the case of As donors include the stress dependence of the individual valley functions $\Phi_j^{(1)}$.

The conclusions drawn by Wilson and Feher from their experimental data remain correct since they employed only moderate stresses. An extension of their measurements to saturation stresses could determine the correct stress dependence of $\Phi_1^{(1)}(0)$ and possibly the stress dependence of the valley-orbit splitting parameter Δ, mentioned at the end of Sec. II.

In addition to the decrease of the hyperfine splitting, Wilson and Feher observed[18] in As-doped germanium a motional narrowing of the spin resonance lines as they increased the stress. This effect is due to the increase in overlap and hence of the interaction between neighboring impurity states. It agrees with the decrease of the resistivity of impurity conduction under [111] compression. In the case of Sb-doped germanium the opposite should occur; the motional narrowing observed at certain impurity concentrations at zero stress should disappear at large [111] compressions.

ACKNOWLEDGMENTS

It is a pleasure to thank M. H. Cohen and W. D. Twose for many fruitful discussions throughout this work.

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[17] W. D. Twose (private communication).

[18] D. K. Wilson (private communication).

APPENDIX. EFFECTIVE MASS APPROXIMATION[18a]

The purpose of this Appendix is to emphasize the assumptions on which the usual effective-mass treatments[3] of the impurity wave function are based, and to indicate the derivation of Eqs. (3) and (8) containing corrections to this approximation in a form suitable for interpretation of strain experiments.

The donor wave function is written as a sum of Bloch functions

$$\Psi(\mathbf{r})=\sum_n \int_{\mathrm{B.Z.}} d^3k\, C_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}). \qquad \text{(A1)}$$

The subscript n labels the conduction bands. Let H be the Hamiltonian of an electron in the conduction band (with no impurity present), so that

$$H\psi_{n\mathbf{k}}=E_n(\mathbf{k})\psi_{n\mathbf{k}},$$

and let $V(r)$ be the impurity ion potential. Then the coefficients $C_n(\mathbf{k})$ satisfy

$$[E_n(\mathbf{k})-E]C_n(\mathbf{k}) + \sum_{n'}\int_{\mathrm{B.Z.}} d^3k' \int d^3r\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}u^*_{n\mathbf{k}}(\mathbf{r})u_{n'\mathbf{k}'}(\mathbf{r}) \times V(r)C_{n'}(\mathbf{k}')=0, \qquad \text{(A2)}$$

where E is the energy of the donor electron. It is known[3] that a good solution to (A2) is obtained by considering the lowest conduction band only ($n=0$), and expanding $E_0(\mathbf{k})$ to order k^2 about each minimum. Defining the envelope function

$$F_j(\mathbf{r})=\int d^3k\, e^{i(\mathbf{k}-\mathbf{k}_j)\cdot\mathbf{r}}C_0(\mathbf{k}-\mathbf{k}_j), \qquad \text{(A3)}$$

where $\mathbf{k}_j$ is the wave vector to the jth minimum, Kohn and Luttinger[3] find an impurity wave function of the form of Eq. (1), with $F_j(\mathbf{r})$ satisfying the effective-mass equation,

$$[H_j-E]F_j(\mathbf{r})\equiv[\mathbf{p}\cdot\mathbf{A}_j\cdot\mathbf{p}+V(r)-E]F_j(\mathbf{r})=0. \qquad \text{(A4)}$$

$\mathbf{A}_j$ is the inverse effective-mass tensor appropriate to the jth minimum, and $\mathbf{p}$ is the momentum. $C_0(\mathbf{k})$ has appreciable magnitude only in a range $\Delta k\sim\pi/a_H$ about each conduction band minimum, where a_H is the average impurity Bohr radius, since, from Eq. (2),

$$F(\mathbf{r})\sim e^{-r/a_H}.$$

Hence integrals containing $C(\mathbf{k})$ can in general be extended over all k space with negligible error.

A slightly more complete equation defining $F_j(\mathbf{r})$ is given below. For the purposes of a later brief discussion, we list the assumptions made in its derivation; these are all implicit in earlier treatments. I. $V(r)$ varies slowly over a distance of order the lattice spacing c. II. Only the lowest conduction band $n=0$ is considered. III. $u_{0\mathbf{k}}(\mathbf{r})$ is independent of $\mathbf{k}$ in a range $\Delta k\sim\pi/a_H$ about each minimum at $\mathbf{k}_j$. IV. $E_0(\mathbf{k})$ is expanded to order k^2 about each $\mathbf{k}_j$. Then (A2) becomes

$$[E_0(\mathbf{k})-E]C_0(\mathbf{k}) + \int d^3k' \int d^3r\, e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}V(r)C_0(\mathbf{k}'). \qquad \text{(A5)}$$

Putting

$$C_0(\mathbf{k})=\sum_j \alpha_j C_j(\mathbf{k}-\mathbf{k}_j),$$

multiplying by $e^{i(\mathbf{k}-\mathbf{k}_j)\cdot\mathbf{r}}$, and integrating over r, we obtain

$$[H_j-E]\alpha_jF_j(\mathbf{r}) + \sum_{l\neq j}\alpha_l e^{i(\mathbf{k}_l-\mathbf{k}_j)\cdot\mathbf{r}}[H_l-E]F_l(\mathbf{r})=0. \qquad \text{(A6)}$$

H_j is as defined in (A4). The second group of terms on the left arises because $C_l(\mathbf{k}-\mathbf{k}_l)$ is large about $\mathbf{k}_l$ only. The α_j are numerical coefficients determined by the requirement that the total donor wave function [(A1) or (1)] have the tetrahedral symmetry of the lattice.

It is interesting to note that even in this approximation there is a small splitting of the fourfold-degenerate donor ground state. The 4×4 secular determinant obtained from (A6) has equal diagonal elements $d-E=\langle F_j|H_j|F_j\rangle-E$ and equal off-diagonal elements $g-Eh=\langle F_l e^{i(\mathbf{k}_l-\mathbf{k}_j)\cdot\mathbf{r}}|H_j-E|F_j\rangle$. There is one threefold-degenerate solution

$$E=(d-g)/(1-h),$$

and one nondegenerate solution

$$E=(d+3g)/(1+3h).$$

Since contributions to g and h come only from regions of space where $(\mathbf{k}_l-\mathbf{k}_j)\cdot\mathbf{r}\lesssim 1$, and $|\mathbf{k}_l-\mathbf{k}_j|\sim K$, a reciprocal lattice vector, these are essentially central cell corrections to E and $F(\mathbf{r})$.

The inclusion of strain effects into (A6) is straightforward. Using the deformation potential approximation,[13] matrix elements of the strain are diagonal in the Bloch functions ψ_{nk}; hence to each H_j we must add a strain energy ϵ_j representing the shift of each conduction band minimum. The "symmetry" coefficients α_j are, however, now strain dependent also.

The main error in (A6) lies in assumption I, as emphasized by Kohn and Luttinger.[19] In fact $V(r)$ varies rapidly in the central cell, due both to the Coulombic nature of the potential near the impurity ion and breakdown of the concept of a dielectric constant κ in that region. Equation (A6) can be cor-

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[18a] The Appendix is by W. D. Twose, Institute for the Study of Metals, University of Chicago, Chicago, Illinois.

[19] W. Kohn and J. M. Luttinger, Phys. Rev. 97, 883 (1955).

rected by writing

$$V(r)=-e^2/\kappa r+U(r),$$

where $U(r)$ is a correction potential localized in the central cell. We can suppose it to consist of two terms; $+e^2/\kappa r$ in the central cell only, and a term $v(r,\theta,\phi)$ which contains the detailed nature of the central cell potential and depends on the type of impurity ion (see Sec. II). The correction term to (A6) can be written approximately

$$\textstyle\sum_j U(r)\alpha_j F_j(0),$$

since $U(r)$ is sharply localized. The complete equation for F_j, including strain, is then

$$[H_j+\epsilon_j-E]\alpha_j F_j(\mathbf{r})+\sum_{j\neq l} e^{i(\mathbf{k}_j-\mathbf{k}_l)\cdot\mathbf{r}}[H_j+\epsilon_j-E]\alpha_j F_j(\mathbf{r}) +\sum_j U(r)\alpha_j F_j(0)=0. \quad \text{(A7)}$$

It is fairly readily seen that the effects of higher bands may be included in the correction potential $U(r)$. Physically this is due to the strong impurity potential near the ion mixing Bloch functions from higher bands into the impurity wave function. Using an interation procedure on (A2),

$$C_n(\mathbf{k})\sim\frac{1}{E_n-E}\int d^3k'\int d^3r\ V(r)e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}C_0(\mathbf{k}'),$$

and on substituting this into (A5) an extra term is obtained in (A7) approximately of the form

$$\sum_n \frac{1}{E_n-E}[V(r)]^2F(\mathbf{r}),$$

which is essentially a "contact" term since $V^2(r)$ is small except near $r=0$. This term will introduce a small strain dependence into $U(r)$, since E_n-E is a function of strain.

Corrections to F_j due to the departure of $E_0(k)$ from quadratic are of order c/a_H or smaller, where c is the lattice spacing. For example, assuming a band of the form $E_0(\mathbf{k})\propto\sin^2(\mathbf{k}-\mathbf{k}_j)\cdot\mathbf{c}$ leads to a corrected effective-mass Hamiltonian

$$H_j\simeq[1+\tfrac{1}{3}(c/a_H)^2]\mathbf{p}\cdot\mathbf{A}_j\cdot\mathbf{p}-e^2/\kappa r.$$

The **k**-dependence of the periodic part of the Bloch function, $u_{n\mathbf{k}}(\mathbf{r})$, is unimportant for determining the form of H_j, since only the immediate neighborhood of a band minimum need be considered. However, any attempt to go beyond the empirical form of $U(r)$ introduced by Kohn and Luttinger[19] would necessitate knowing $u_{\mathbf{k}}$ over the whole Brillouin zone due to the sharply localized nature of $U(r)$. It is probably not sufficient to regard $u_{\mathbf{k}}$ as independent of $\mathbf{k}$, since the Fourier components of the charge density vary strongly throughout the Brillouin zone due to the covalent bonding in group IV semiconductors (see, for example, Phillips and Kleinman,[20] who have studied the charge density in diamond).

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[20] L. Kleinman and J. C. Phillips, Bull. Am. Phys. Soc. **6**, 109 (1961).