

becomes

$$I = E_3 C(V) \int_{E_1}^{E_3} dE E^{1/2} e^{E/E_3}. \quad (C2)$$

The restriction $E/E_3 > 1$ can be written equivalently as

$$E/E_0 > 2/\ln(V_B/E_0). \quad (C3)$$

If electrons of energy E less than set by this inequality are important in the tunneling process then the angular integrals must be included and a $E^{3/2}$ rather than $E^{1/2}$ dependence then applies.

The WKB solution for the parabolic barrier is equal to the exact solution of CDMT for

$$E > 4E_0. \quad (C4)$$

This can be seen by rewriting Eq. (9) of CDMT in a form appropriate to this limit and comparing terms with the integral form of Appendix B. For $E > 4E_0$ the tunneling is not proportional to the density of states, and the conclusions of Harrison²⁸ pertain.

The range in energy over which the integrand in the expression for tunneling must include the density of states factor $E^{1/2}$ is from Eqs. (C3) and (C4)

$$4 > E/E_0 > 2/\ln(V_B/E_0). \quad (C5)$$

For n -type GaAs at $n_0 = 10^{19} \text{ cm}^{-3}$, $E_0 \sim 0.07 \text{ eV}$ and $V_B = 0.92 \text{ eV}$ the range in energy becomes

$$0.28 \text{ eV} > E > 0.07 \text{ eV}. \quad (C6)$$

This is the range which is significant in the tunneling processes of interest.

Stress Dependence of Photoluminescence in GaAs

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Photoluminescence in GaAs at $k=0$ under uniaxial stress up to $14\,000 \text{ kg/cm}^2$ is studied at 2°K . The stress dependence of the coupling between $J = \frac{3}{2}$, $m_j = \pm \frac{3}{2}$ and $J = \frac{1}{2}$, $m_j = \pm \frac{1}{2}$ valence bands is observed. The deformation-potential constants for the valence band and for the acceptor ground state are determined, and the values for the valence band are $a = -8.9 \text{ eV}$, $b = -1.96 \text{ eV}$, and $d = -5.4 \text{ eV}$.

I. INTRODUCTION

THE application of uniaxial stress to a semiconductor shifts the energy extrema. The top of the valence band in GaAs, which is fourfold degenerate at $k=0$ at zero stress, splits into two doubly degenerate components. There will also be changes in the ionization energy of impurity levels. Since the conduction band is nondegenerate, these changes for shallow donor levels are expected to be small compared to energy-gap changes. In contrast, since the valence-band degeneracy is removed, changes in shallow acceptor ionization energies are expected to be comparable to energy-gap changes.¹

Studies of the stress dependence of the photoluminescent spectra near the energy gap can be used to determine deformation-potential constants. Because of the large stress effect on acceptor levels, the stress dependence of the spectrum can also be used to determine whether or not an acceptor level is involved in a particular transition. Such studies have been carried out on GaAs photoluminescent spectra for stress χ applied in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions at 2°K . Two lines have been studied: line A at 1.511 eV and line B at 1.490 eV . Our results support the hypothesis that

line A does not involve an acceptor level but line B does. This is consistent with the results of Leite and Di Giovanni² who attributed line B to a donor-acceptor pair transition. At low stresses, the variation in band-gap energy E_g is linear in χ .³ However, at high stresses, a quadratic dependence of E_g on χ is expected⁴⁻⁶ from a stress-induced coupling between the top of the valence band and the deep lying spin-orbit split-off band. Both linear and quadratic terms are then used to obtain the deformation potential constants.

II. EXPERIMENTAL METHODS AND RESULTS

The arrangement for the photoluminescent measurements has already been described elsewhere.⁷ A compressive stress up to $14\,000 \text{ kg/cm}^2$ on the sample was applied with an apparatus similar to one described by

² R. C. C. Leite and A. E. Di Giovanni, *Phys. Rev.* **153**, 841 (1967).

³ G. E. Pikus and G. L. Bir, *Fiz. Tver. Tela* **1**, 1642 (1959) [*English transl.: Soviet Phys.—Solid State* **1**, 1502 (1959)].

⁴ H. Hasegawa, *Phys. Rev.* **129**, 1029 (1963).

⁵ J. C. Hensel and G. Feher, *Phys. Rev.* **129**, 1041 (1963).

⁶ A. P. Smith, M. Cardona, and F. H. Pollak, *Bull. Am. Phys. Soc.* **12**, 101 (1967).

⁷ M. I. Nathan and G. Burns, *Phys. Rev.* **129**, 125 (1963). A He-Ne laser was used for excitation of the spectra.

¹ P. J. Price, *Phys. Rev.* **124**, 713 (1961).

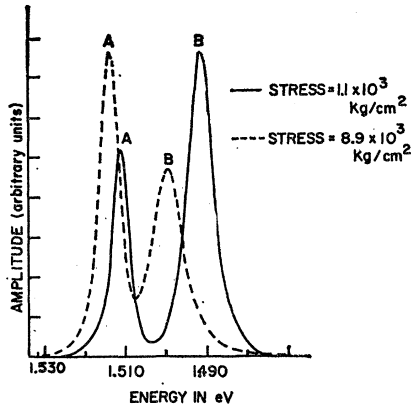


FIG. 1. Photoluminescent spectra at 2°K in *n*-type GaAs No. 38 DHA, $n=6 \times 10^{15}/\text{cc}$, at two values of stress.

Cuevas and Fritzsche⁸ and stresses were measured by a linear variable differential transformer and a null indicator. All the measurements were made at $\approx 2^\circ\text{K}$. Typical samples of dimensions 8 mm \times 1.2 mm \times 1.0 mm were polished optically flat and parallel at the ends as described by Hall.⁹ Two crystals extensively studied were (1) *n*-type No. 38 DHA $n=6 \times 10^{15}/\text{cc}$ and (2) *p*-type No. 1120 $n=1 \times 10^{17}/\text{cc}$. Other crystals had similar behavior. Typical spectra observed in *n*-type samples are shown in Fig. 1. The stress dependence of the energy of the peak of both the lines for stress in $\langle 111 \rangle$ is shown in Fig. 2, and the stress dependences of the peak of line A for $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ stress directions are compared in Fig. 3. The breaking stress

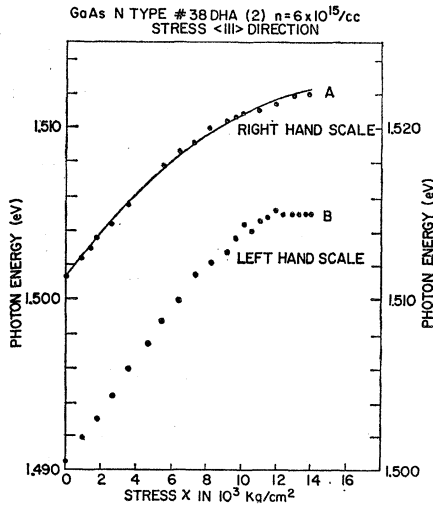


FIG. 2. The photon energy of the photoluminescence peak versus stress in the $\langle 111 \rangle$ direction at 2°K in *n*-type GaAs, No. 38 DHA $n=6 \times 10^{15}/\text{cc}$. The solid line for line A is the theoretical fit, using Eq. (3b) with the chosen values of $a=-8.9$ eV and $d=-5.4$ eV. The value of the initial slope of line B determines the effective deformation potential d' for the acceptor level. (see Table I).

⁸ M. Cuevas and H. Fritzsche, Phys. Rev. 137, A1847 (1965). We are indebted to Dr. F. H. Pollak for advice and discussions concerning the apparatus.

⁹ J. J. Hall, Phys. Rev. 128, 68 (1962).

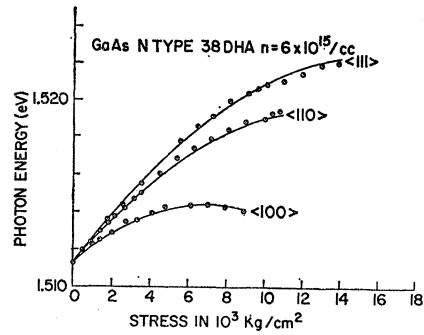


FIG. 3. The dependence of the photon energy of line A on stress. The points are experimental. The curves are calculated, using Eq. (3b) and the best-fit values of a , b , and d shown in Table I.

in all the three directions corresponded to a strain $\approx 1.2\%$. The stress dependence of lines A and B have qualitatively similar behavior. In the low-stress region, the peak shift with stress is larger for line B as compared to line A (see Fig. 2). These different slopes are used to obtain the deformation-potential constants for the valence band and for the acceptor ground state as shown later.

The data on the *p*-type crystal show only one line, corresponding to line B, of photon energy 1.484 eV. We also observe an increase in the intensity of line A and a simultaneous decrease in the intensity of line B with increasing stress (Fig. 1). This may be due to the change of the capture cross section for the acceptor level with stress.

III. THEORY AND DISCUSSION

We shall now discuss theoretically the stress dependence of the valence band and the ground state of the acceptor state and compare our experimental results with theory.

A. Valence Band

The valence-band Bloch states at $k=0$, which are formed from three *p*-like orbitals, consist of a four-fold

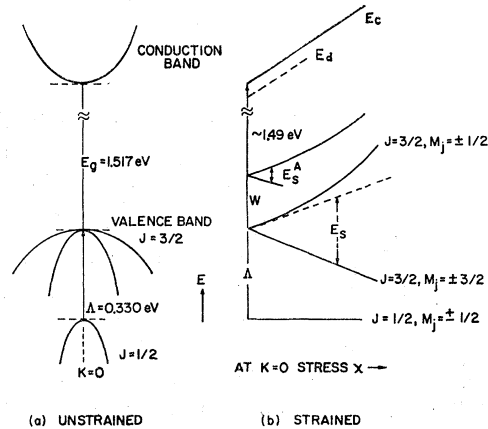


FIG. 4. Band structure of GaAs for the lowest conduction band and highest valence band and its stress dependence.

TABLE I. The deformation-potential coefficients for the conduction and valence band and the ground state of acceptor levels in GaAs.

	Experimental values ^a (eV)					Theoretical values for $\Lambda = \infty$ ^b				Emtage's ^c calc. value $b'/b=d'/d$
	<i>a</i>	Valence band		Acceptor level		Si		Ge		
		<i>b</i>	<i>d</i>	<i>b'/b</i>	<i>d'/d</i>	<i>b'/b</i>	<i>d'/d</i>	<i>b'/b</i>	<i>d'/d</i>	
<i>n</i> type	-8.9	-1.96	-5.4	0.56	0.88	0.77	0.82	0.56	0.61	0.2
<i>p</i> type	0.67	0.75					

^a Estimated errors in the determination of *a*, *b*, and *d* are less than 5%.

^b See Ref. 18.

^c See Ref. 21.

degenerate $J = \frac{3}{2}$ state and a two-fold degenerate $J = \frac{1}{2}$ state separated by spin-orbit splitting $\Lambda = 0.33$ eV [Fig. 4(a)].¹⁰ Under uniaxial compression, the degeneracy of the $J = \frac{3}{2}$ state is partially removed to two doubly degenerate states with $m_j = \pm \frac{3}{2}$ and $m_j = \pm \frac{1}{2}$, respectively. It is known^{5,11} that under compressive stress $m_j = \pm \frac{1}{2}$ state moves up and $m_j = \pm \frac{3}{2}$ state moves down with respect to their center of gravity as shown in Fig. 4(b). The splitting energy E_s between $J = \frac{3}{2}$, $m_j = \pm \frac{1}{2}$ and $J = \frac{3}{2}$, $m_j = \pm \frac{3}{2}$ has been calculated to the first order in stress χ by Pikus and Bir³ (henceforth referred to as PB) with coefficients involving the appropriate deformation-potential constants. In computing the linear dependence of E_s on χ , PB neglected the presence of the $J = \frac{1}{2}$, $m_j = \pm \frac{1}{2}$ band completely. However, at high stresses, since E_s is not $\ll \Lambda$, one should include the contribution due to stress-induced changes of the interaction of $J = \frac{1}{2}$ and $J = \frac{3}{2}$ bands. We have extended the above calculation to the next order of the perturbation series.

To compute the stress dependence of the valence-band edge, we treat stress as a perturbation similar to the $\mathbf{k} \cdot \mathbf{p}$ approximation. The electron energies are the eigenvalues of a 6×6 matrix, most conveniently expressed here in the representation which diagonalizes the spin-orbit coupling.^{12,13} The elements of this matrix involve a linear combination of the familiar Shockley matrix¹⁴ and a similar perturbation matrix D due to strain given by Eq. (1) of PB. The elements of D are linear in strain ϵ and the coefficients are linear combinations of the deformation-potential constants. Since we are interested in $k=0$, the Shockley matrix does not contribute. For computing the linear dependence on ϵ , one can then approximate the 6×6 matrix D by considering only the elements in the 4×4 block in the upper left corner and the 2×2 block in the lower right corner. The results for the 4×4 matrix given by Eq. (14) in PB are

$$\Delta(E_c - E_v) = a(S_{11} + 2S_{12})\chi \pm \frac{1}{2}E_s, \quad (1)$$

where E_s is the linear term of the splitting energy between $J = \frac{3}{2}$, $m_j = \pm \frac{1}{2}$ and $J = \frac{3}{2}$, $m_j = \pm \frac{3}{2}$ band given by

$$\begin{aligned} (E_s)_{100} &= 2b(S_{11} - S_{12})\chi, \\ (E_s)_{111} &= (dS_{44}/\sqrt{3})\chi, \\ (E_s)_{110} &= \{b^2(S_{11} - S_{12})^2 + \frac{1}{4}d^2S_{44}^2\}^{1/2}\chi, \end{aligned} \quad (2)$$

where a is the hydrostatic pressure deformation potential for the energy gap; b and d are the deformation potentials appropriate to strains of tetragonal and rhombohedral symmetries, respectively; S_{11} , S_{12} , and S_{44} are elastic compliance coefficients.¹⁵ In Eq. (1) the positive sign is for the $m_j = \pm \frac{3}{2}$ and the negative sign for the $m_j = \pm \frac{1}{2}$ states, and the stress is taken to be positive for tension. The elements in the two 2×4 strips in the matrix D affect the roots to χ^2 and higher orders. From the degenerate perturbation theory to the second order,¹⁶ we obtain the quadratic stress dependence for the two states:

$$\Delta(E_c - E_v)_{m_j = \pm 3/2} = a(S_{11} + 2S_{12})\chi + \frac{1}{2}E_s, \quad (3a)$$

$$\Delta(E_c - E_v)_{m_j = \pm 1/2} = a(S_{11} + 2S_{12})\chi - \frac{1}{2}E_s(1 + E_s/\Lambda). \quad (3b)$$

Line A has previously been attributed to a free or a bound exciton transition.² In either case, it is reasonable to fit the data to Eq. (3b). The best theoretical fit, as shown by the solid line in Fig. 3, was obtained for the choice of a , b , and d given in Table I. Values of a , b , and d so obtained are slightly different from those obtained by the electroreflectance technique where the authors¹¹ neglected the quadratic term in Eq. (3b) and made the measurements at room temperature. Our value of a is in very good agreement with the value of -9.0 eV obtained by hydrostatic pressure measurements.¹⁷

B. Acceptor Level

The stress dependence of the ground state of an acceptor level for low stress (where the strain splitting energy between the two acceptor states is much less than the acceptor binding energy) has been investigated by Bir, Butikov, and Pikus.¹⁸ They have computed the expectation value of the strain Hamiltonian using the acceptor wave functions as obtained by Schechter¹⁹ by a variational method. The energy changes so obtained can be expressed in terms of the acceptor-state effective-

¹⁵ For the values of the elastic compliance coefficients used see O. Madelung, *Physics of III-V Compounds* (John Wiley & Sons, Inc., New York, 1964), p. 345.

¹⁶ Cf., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 154.

¹⁷ W. Paul, *J. Appl. Phys.* **32**, 2082 (1961).

¹⁸ G. L. Bir, E. I. Butikov, and G. E. Pikus, *J. Phys. Chem. Solids* **24**, 1467 (1963).

¹⁹ D. Schechter, *J. Phys. Chem. Solids* **23**, 237 (1962).

¹⁰ A. G. Thompson, M. Cardona, K. L. Shaklee, and J. C. Woolley, *Phys. Rev.* **146**, 601 (1966).

¹¹ F. H. Pollak, M. Cardona, and K. L. Shaklee, *Phys. Rev. Letters* **16**, 942 (1966).

¹² G. Dresselhaus, A. F. Kip, and C. Kittel, *Phys. Rev.* **98**, 368 (1955).

¹³ E. O. Kane, *J. Phys. Chem. Solids* **1**, 82 (1956).

¹⁴ W. Shockley, *Phys. Rev.* **78**, 173 (1950).

deformation-potential constants a' , b' , and d' , similar to the valence-band deformation-potential constants. Since the impurity level is shifted together with the band edge in hydrostatic compression, $a = a'$, which has been experimentally confirmed.^{17,20} The results of Bir *et al.*¹⁸ for Ge and Si for the case $\Lambda = \infty$, and measured values of b' and d' for the acceptor-state transition for GaAs (line B) are listed in Table I. The initial slope in the low-stress region is used to obtain b' and d' . The theoretical values for GaAs cannot be computed because the effective-mass parameters have not been determined. The experimental values obtained for GaAs are reasonably close to the theoretical values for Si and Ge. Another theoretical study²¹ pertaining to the measurements of peak shift with stress of GaAs *p-n* junction luminescence²² gave $b'/b = d'/d = 0.2$. These values do not fit our data. We observe, in the case of line B, a small difference in the peak energies in the components polarized parallel and perpendicular to the stress direction. The observed effect is inconsistent

²⁰ J. Feinleib, S. Groves, W. Paul, and R. Zallen, *Phys. Rev.* **131**, 2070 (1963).

²¹ P. R. Emtage, *J. Appl. Phys.* **36**, 1408 (1965).

²² R. C. Miller, F. M. Ryan, and P. R. Emtage, in *Proceedings of the 7th International Conference on Semiconductor Physics, Paris, 1964* (Academic Press Inc., New York, 1965).

with the explanation given by Emtage,²¹ who attributed the above transitions to the two doubly degenerate states of $J = \frac{3}{2}$ multiplet of the acceptor level.

IV. CONCLUSION

We conclude from the study of the stress dependence of the luminescent spectra of GaAs that line A does not involve an acceptor state whereas line B does. Both linear and quadratic stress dependences are used to obtain the deformation-potential constants for the line A. The deformation-potential constants obtained from the linear slope in the low-stress region in the case of an acceptor state are consistent with the theoretical estimate made using valence-band parameters for Ge and Si in the limit of large spin-orbit splitting.¹⁸ More complete comparison of theory and experiment must await determination of valence-band parameters for GaAs.

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Irradiation Damage in *n*-Type Germanium at 4.2°K*†

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The conductivity measured during the application of pulsed electric fields is used to monitor the damage introduced at 4.2°K by energetic electron irradiation of *n*-type germanium. Fields above about 20 V/cm completely ionize the donor impurities. Radiation-induced defects deplete the electron population of the donors by introducing deeper acceptor levels. A sensitivity to defect concentrations of 10^{12} cm⁻³ is obtained in material containing about 10^{14} Sb impurities cm⁻³. The introduction rates of various defects are studied as a function of irradiation energy. One type, previously identified as a close vacancy-interstitial pair, is removed (presumably by annihilation) in the order of minutes by annealing at 65°K. This defect accounts for 95% of the conductivity change produced by irradiation at 0.7 MeV, but only 50% of the change at 4.5 MeV. Evidently this is the primary defect requiring the least energy for its formation. A second type of primary defect is distinguished by the fact that it is present after annealing to 90°K. The dependence on bombardment energy of the introduction rate of this defect indicates that multiple displacements may be involved in its production, and therefore it may be a double vacancy. A third type of defect is observed only after large fluxes of low-energy electrons, and appears to be a secondary defect resulting from radiation-induced conversion of primary defects. This defect also remains after annealing to 90°K, but it has electrical properties very similar to those of the defect that anneals at 65°K. Trapping properties of the first and third defect types lead to the conclusion that they are both capable of capturing two electrons in *n*-type germanium and are therefore double-acceptor centers.

I. INTRODUCTION

ELECTRICAL measurements provide a very sensitive means of detecting damage centers introduced into germanium by energetic electron irradiation.

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Radiation defects change the population of carriers by introducing donor or acceptor levels into the forbidden gap. Above about 30°K in lightly doped *n*-type germanium, small changes in carrier concentration due to the introduction of defects with energy levels below the Fermi energy are given by

$$\Delta n = \sum_i \delta_i N_i, \quad \Delta n/n_0 \ll 1, \quad (1)$$