

Strain Dependence of the Acceptor Binding Energy in Diamond-Type Semiconductors

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It is shown that if the acceptor binding energy be expanded in inverse powers of the strain amplitude, $W(\epsilon) = W(\infty) + W_1/\epsilon + \dots$, then the product $E_S W_1/\epsilon$, where E_S is the strain-induced splitting of the band edge, may be equated to a certain (constant) quantity, Z_0 , which is readily calculable in terms of the infinite-strain acceptor ground state. Z_0 is calculated for germanium with an uniaxial [100] compression. A provisional value of W_1 , obtained from the existing data for this case, then gives the result $b=2.9$ eV for the applicable deformation potential constant. An approach to the calculation of W for arbitrary ϵ is suggested.

It has been shown by Pikus and Bir¹ that the degeneracy at the valence band edge in the semiconductors typified by germanium is lifted by a shear strain, the resulting energy functions being of the simple "valley" type²:

$$E(\mathbf{k}) = \begin{cases} -\frac{1}{2}E_S + \frac{1}{2}\hbar^2\mathbf{k}\cdot\boldsymbol{\gamma}_A\cdot\mathbf{k}, \\ +\frac{1}{2}E_S + \frac{1}{2}\hbar^2\mathbf{k}\cdot\boldsymbol{\gamma}_B\cdot\mathbf{k}, \end{cases} \quad (1)$$

for small \mathbf{k} . The reciprocal-mass tensors $\boldsymbol{\gamma}_A$ and $\boldsymbol{\gamma}_B$ are functions of the relative values of the strain components ϵ_{ij} , and independent of the strain amplitude ϵ . The splitting E_S is proportional to ϵ (that is, E_S is a linear homogeneous function of the ϵ_{ij}). The result expressed by (1) has been directly verified by observation of cyclotron resonance in silicon.³ In germanium, the variation of the Hall mobility, as a function of ϵ , from the zero-strain limit to the large-strain limit has been demonstrated, and what appears to be most of the corresponding curve for acceptor binding energy was also obtained.⁴ The scales of these two curves provide a very rough measure of the applicable deformation-potential element (the transition between the limiting small-strain and large-strain values should occur at strains where kT and the acceptor binding energy, respectively, equal E_S in order of magnitude), but there is no immediate prospect of getting at all accurate measures in this way. Even if data representing only acoustic-phonon scattering could be obtained, the theory of the mobility, though simple in the large-strain limit,⁵ is very complicated for zero strain^{6,7} and a satisfactory theory for the intermediate range would be even more complicated. The situation is similar, though not as bad, for the acceptor binding energy, W . It is shown below, however, that for W the theory of the approach to the large-strain

limit is straightforward and quite tractable and that, at least on the basis of the effective mass approximation,⁸ the results may be used to derive the deformation-potential elements from suitable data. What is calculated is the second term of the expansion

$$W(\epsilon) = W(\infty) + W_1/\epsilon + \dots \quad (2)$$

The effect of the strain is⁹ to add to the Shockley matrix terms proportional to the ϵ_{ij} . The complete matrix of the band-edge part of this system (i.e., after the usual separation of the band split off by spin-orbit coupling¹⁰) may then be transformed so that the strain terms are diagonal¹¹:

$$H = \begin{pmatrix} -\frac{1}{2}E_S + H_A & H_{AB} \\ H_{AB}^\dagger & +\frac{1}{2}E_S + H_B \end{pmatrix}, \quad (3)$$

where the strain terms are $\pm\frac{1}{2}E_S$. Since the strain terms⁹ are independent of \mathbf{k} , so is the transformation to (3). H_A , H_B , and H_{AB} are diagonal in the new Bloch representation (that is, their matrix elements vanish for $\mathbf{k}' \neq \mathbf{k}''$).¹¹ Since H_{AB} may be neglected if E_S is large enough, in diagonalizing (3), $H_A(\mathbf{k})$ and $H_B(\mathbf{k})$ are identical with the second terms in (1). The next approximation, analogous to (2), is

$$E(\mathbf{k}) \simeq \begin{cases} -\frac{1}{2}E_S + H_A(\mathbf{k}) - Z(\mathbf{k})/E_S, \\ +\frac{1}{2}E_S + H_B(\mathbf{k}) + Z(\mathbf{k})/E_S, \end{cases} \quad (4)$$

where

$$Z(\mathbf{k}) = |H_{AB}(\mathbf{k})|^2. \quad (5)$$

⁸ W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

⁹ E. N. Adams, Chicago Midway Laboratories Report CML-TN-P8, 1954 (unpublished).

¹⁰ Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955). Also reference 9.

¹¹ The "two-by-two" form of (3) signifies division of the complete function space into "A" and "B" spaces. There are two independent states in each space for each value of \mathbf{k} , in the Bloch representation, since the Kramers degeneracy is not lifted by the strain. The $Z(\mathbf{k})$ are, precisely speaking, the eigenvalues of $H_{AB}H_{AB}^\dagger$, which depend on \mathbf{k} only (that is, they are doubly degenerate). The eigenvalues of $H_{AB}^\dagger H_{AB}$ are equal, for each value of \mathbf{k} , to those of $H_{AB}H_{AB}^\dagger$. (When we refer later to the quantum operator Z , we mean $H_{AB}H_{AB}^\dagger$ with reference to the A space and $H_{AB}^\dagger H_{AB}$ with reference to the B space.) This degeneracy complication is overlooked, for simplicity, in the derivation of (9). The latter is correct, all the same, with $Z(\mathbf{k})$ defined by (4) and with (8) referring equally to either one of the two sets of Bloch states belonging to the A space. Similarly for (26) and (28).

¹ G. E. Pikus and G. L. Bir, Soviet Phys.-Solid State **1**, 1502 (1960).

² Here, and throughout, the signs of energies are proper to holes rather than to electron states. The contribution from the dilation, $\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$, to all energies is dropped here and throughout this paper.

³ L. C. Hensel and G. Feher, Phys. Rev. Letters **5**, 307 (1960).

⁴ S. H. Koenig and J. J. Hall, Phys. Rev. Letters **5**, 550 (1960).

⁵ P. J. Price and Yi-Han Kao, IBM J. Research Develop. **5**, 63 (1961).

⁶ G. L. Bir and G. E. Pikus, Soviet Phys.-Solid State **2**, 2039 (1961).

⁷ M. Tiersten, IBM J. Research Develop. **5**, 122 (1961).

The acceptor bound states are the eigenstates of $H+U(\mathbf{r})$, where $U(\mathbf{r})$ is the acceptor ion potential. We now establish as basis states the eigenstates of $H+U$ subject to the constraint that their wave functions ψ_{A_n} ($n=0, 1, 2, \dots$) are linear combinations of the Bloch state functions φ_{A_k} of the "A" space only, and similarly ψ_{B_n} for the "B" system. (That is, ψ_{A_0} minimizes the expectation of $H+U$ subject to the constraint, ψ_{A_1} minimizes it with the additional restriction of being orthogonal to ψ_{A_0} , and so on.) Let the stationary energies be $-\frac{1}{2}E_S - W_{A_n}$ and $+\frac{1}{2}E_S - W_{B_n}$. The ψ_{A_n} , ψ_{B_n} , W_{A_n} , and W_{B_n} will all be independent of strain and E_S . We are completely neglecting the influence of all other bands (i.e., their coupling to the system by matrix elements of U), and therefore the ψ_{A_n} are eigenfunctions of $H+U$, and the W_{A_n} corresponding binding energies, in the limit of large ϵ and E_S . In particular, $W(\infty) = W_{A_0}$.

The present procedure is analogous to that in the author's theory of the strain dependence of the donor ground state in germanium and silicon,¹² but the circumstances are different here. The matrix elements of H_{AB} (between the ψ_A and the ψ_B) will be comparable with the matrix elements of H_A+U and H_B+U , and the effect of the former is small only because (and when) E_S is large compared with them. On the other hand, the AB matrix elements of U (the equivalent of which have a dominant role in the donor case¹²) may be expected to be small compared with those of H_{AB} when, at the large-strain limit, the "chemical shift" deviation of the binding energy $W(\infty)$ from the value calculated by the effective mass approximation⁸ is fractionally small. The AB elements of U are neglected below.

We now include the effect of H_{AB} by second-order perturbation theory. The change in the acceptor binding energy is, to this order,

$$W(\epsilon) - W(\infty) \simeq \sum_n \frac{(\psi_{A_0} | H | \psi_{B_n})(\psi_{B_n} | H | \psi_{A_0})}{E_S + W_{A_0} - W_{B_n}}, \quad (6)$$

where the sum is to be understood as including the nonbound states in the B space. It is now evident that the second term of (2) is to be obtained by replacing the denominator of (6) by E_S . Then

$$W_1/\epsilon = (\psi_{A_0} | H \mathcal{G}_B H | \psi_{A_0}) / E_S, \quad (7)$$

where \mathcal{G}_B is the identity operator of the B function space. Let

$$\psi_{A_n} = \sum_k a_{nk} \varphi_{A_k}. \quad (8)$$

Then the numerator on the right of (7) becomes

$$\sum_k |a_{0k}|^2 |H_{AB}(\mathbf{k})|^2.$$

Therefore, by (5),

$$W_1/\epsilon = (1/E_S) \sum_k Z(\mathbf{k}) |a_{0k}|^2. \quad (9)$$

To include the effect of AB matrix elements of U (associated with the "chemical shift" effect,⁸ and coming from the neighborhood of the acceptor atom), one should replace H in (6) and (7) by $H+U$.

In the effective mass approximation⁸ one describes the bound states by slowly varying "envelope wave functions," $\Psi(\mathbf{r})$, which are the eigenfunctions of an effective Schrödinger operator obtained by replacing \mathbf{k} in $U+E(\mathbf{k})$ by $-i\nabla$. Accordingly, in the present case, one calculates the binding energy for the effective Schrödinger operator

$$U(\mathbf{r}) + H_A(-i\nabla) - [Z(-i\nabla)]/E_S \quad (10)$$

to first order in the final term. The W_1 coefficients for the excited states of the A system may evidently be obtained in the same way with (10). The reader is reminded that $Z(\mathbf{k})$ is given by the asymptotic energy functions (4).

As an example, we take the case of a uniaxial stress along the [100] axis:

$$\begin{aligned} \epsilon_{xx} &= -p\epsilon; & \epsilon_{yy} &= \epsilon_{zz} = +rp\epsilon; \\ \epsilon_{xy} &= \dots = 0, \end{aligned} \quad (11)$$

where $p = +1$ for compression, -1 for tension. r is the Poisson's ratio. On substituting (11) into Eq. (14) of reference 1, and suitably expanding the radical in the latter, we find

$$E_S = 2b(1+r)\epsilon, \quad (12)$$

$$H_A(\mathbf{k}) = (A + pB)k_x^2 + (A - \frac{1}{2}pB)(k_y^2 + k_z^2), \quad (13)$$

and

$$\begin{aligned} Z(\mathbf{k}) &= 3B^2(k_y^2 + k_z^2) \left[k_x^2 + \frac{1}{4}(k_y^2 + k_z^2) \right] \\ &\quad + C^2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2). \end{aligned} \quad (14)$$

A , B^2 , and C^2 are the coefficients of the usual expression¹⁰ for the energy function at zero strain:

$$E(\mathbf{k}) = Ak^2 \pm [B^2 k^4 + C^2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{\frac{1}{2}},$$

and b is one of the three deformation potential elements, in the notation of reference 1 (see also references 9 and 5).

We may evaluate W_1 for this case, on the effective mass approximation, with the customary approximation⁸ for the ground-state envelope function:

$$\Psi_0 = (\pi a_{11} a_1^2)^{-\frac{1}{2}} \exp \left[- \left(\frac{x^2}{a_{11}^2} + \frac{y^2 + z^2}{a_1^2} \right)^{\frac{1}{2}} \right]. \quad (15)$$

For $a_{11} = a_1 = a$, the expectation of d^4/dx^4 , etc., would be $1/a^4$, and that of $d^4/dx^2 dy^2$, etc., would be $1/3a^4$. We need only modify these results by the appropriate scale factors $(a/a_{11})^2$ and $(a/a_1)^2$ for each double derivative. Then

$$\begin{aligned} Z_0 &\equiv (\Psi_0 | Z(-i\nabla) | \Psi_0) \\ &= 2B^2 \left(\frac{1}{a_1^4} + \frac{1}{a_{11}^2 a_1^2} \right) + \frac{1}{3} C^2 \left(\frac{1}{a_1^4} + \frac{2}{a_{11}^2 a_1^2} \right). \end{aligned} \quad (16)$$

¹² P. J. Price, Phys. Rev. 104, 1223 (1956).

TABLE I. Data and derived quantities for germanium with a [100] compression.

Atomic units		
Dielectric constant		16.0
<i>A</i>	13.2	
<i>B</i>	+8.9	
<i>C</i>	10.6	
m_1/m_{11}		2.52
a_1	174	
a_{11}	242	
$W(\infty)$	3.15×10^{-4}	4.28×10^{-3} ev
Z_0	3.48×10^{-7}	$64.3 \times (10^{-3}$ ev) ²

It is of interest to apply the result (16) to the case for which Koenig and Hall give experimental data (reference 4, Fig. 2). Following Koenig and Hall, we assume the sign of *B* for which, in their experiment (i.e., for compression), $m_1 > m_{11}$. The values used and the results obtained are given in Table I.¹³

Hall has reanalyzed the data for the sample represented in Fig. 2 of reference 4. A plot of $\log[\sigma(\epsilon)/\sigma(0)]$ against $1/\epsilon$ shows a good straight line for the largest strains, yielding the provisional experimental values¹⁴

$$W(\infty) = 4.6 \times 10^{-3} \text{ ev},$$

$$W_1 = 8.7 \times 10^{-6} \text{ ev.} \tag{17}$$

In view of the uncertainty in the masses used¹⁰ for the theoretical value of $W(\infty)$, and the present uncertainty in the experimental value,¹⁴ the chemical shift could be anything from negligible to about 15%. Applying the above values of Z_0 and W_1 to the relation

$$b = Z_0/2(1+r)W_1, \tag{18}$$

with¹⁵ $r = 0.27$, we obtain the provisional result

$$b = 2.9 \text{ ev.} \tag{19}$$

This value is of course of the expected order of magnitude, though somewhat higher than past estimates (e.g., reference 1). The corresponding calculation and data for a [111] compression should provide the value of the deformation potential constant *d*. (The third constant, Pikus and Bir's *a*, is associated only with the dilation and the resulting equal shift of all levels.²)

Review of the analysis leading to (9) and (18) suggests that the formula

$$W = W(\infty) + Z_0/(E_S + W), \tag{20}$$

¹³ The values of *A*, *B*, and *C* are the final ones in reference 10. The results of R. W. Keyes, IBM J. Research Develop. 5, 65 (1961), were used to calculate a_{11} , a_1 and $W(\infty)$. With the values of *A*, *B*, and *C* given by R. R. Goodman, Phys. Rev. 122, 397 (1961), we obtain 4.25 instead of 4.28 for $W(\infty)$ and 63.3 instead of 64.3 for Z_0 . (These revised values were computed by Mr. Hall.) The changes are not significant here.

¹⁴ J. J. Hall (private communication). The value of $W(\infty)$ is uncertain by about $\frac{1}{4}$ milli ev. A comprehensive experimental investigation of the phenomenon has been initiated, and it is hoped to obtain definitive values of W_1 and $W(\infty)$ for both [100] and [111] compressions.

¹⁵ M. E. Fine, J. Appl. Phys. 26, 862 (1955).

might be a not too bad approximation at smaller strains. The extreme, and presumably least accurate, application of it would be to zero strain, $E_S = 0$, for which (20) gives

$$2W(0) = W(\infty) + [W(\infty)^2 + 4Z_0]^{\frac{1}{2}}. \tag{21}$$

With the values for $W(\infty)$ and Z_0 given in Table I we have, from (21), $W(0) = 10.4 \times 10^{-3}$ ev, compared with Schechter's calculated value 8.9×10^{-3} ev for the same case.¹⁶

A formal theory for the acceptor energy levels at arbitrary strain, involving operations in the A space alone (together with the corresponding analysis for the B space alone, if required), may be approached as follows: We first replace $U(\mathbf{r})$ by the operator, \bar{U} , obtained by setting all AB matrix elements of U equal to zero. After this approximation, we express the complete perturbation-theory series¹⁷ for the *n*th A level in the form

$$W_{An}(E_S) = W_{An}(\infty) + G^A_{nn} + \sum_{s=1}^{\infty} \sum'_{p_1} \sum'_{p_2} \dots \sum'_{p_s} \frac{G^A_{np_1} G^A_{p_1 p_2} \dots G^A_{p_s n}}{(W_{An} - W_{Ap_1}) \dots (W_{An} - W_{Ap_s})}, \tag{22}$$

where

$$G^A_{pq} = \sum_m \frac{(\psi_{Ap} | H_{AB} | \psi_{Bm})(\psi_{Bm} | H_{AB}^\dagger | \psi_{Aq})}{E_S + W_{An} - W_{Bm}}$$

$$= G^A(E_S + W_{An})_{pq}. \tag{23}$$

Again, the summations in (22) and (23) are to be understood as including the non-bound states. In (22) the primes signify as usual that the *n*th level is excluded from the summations. From (22) it may be inferred that the energy levels $-W_{An}$ are the eigenvalues E in the equation

$$\{H_A + \bar{U} - G^A(E_S - E)\} \psi_A = E \psi_A. \tag{24}$$

[If the approximation for U had not been made, H_{AB} in (23) would be replaced by $H_{AB} + U$ but the term \bar{U} in (24) would be unchanged.] The eigenfunctions of (24) belong entirely to the A space, but of course the "dressed" states which they represent belong partly to the B space.

The operator G^A may be represented symbolically as follows:

$$G^A(F) = H_{AB} \left(\frac{1}{F + H_B + \bar{U}} \right) H_{AB}^\dagger. \tag{25}$$

We may write

$$\psi = \psi_A + \psi_B,$$

¹⁶ W. Kohn and D. Schechter, Phys. Rev. 99, 1903 (1955). The difference between the values of *A*, *B*, and *C* used by Schechter and those used in the present paper¹³ presumably makes the disagreement between the two values of $W(0)$ appear slightly less than it actually is.

¹⁷ P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Sec. 9.1.

separating the A-space and B-space parts of the wave function. Then

$$\begin{aligned}(H_A + \bar{U})\psi_A + H_{AB}\psi_B &= E\psi_A, \\ (H_B + \bar{U} + F)\psi_B &= -H_{AB}^\dagger\psi_A.\end{aligned}$$

If we write the second of these two equations, symbolically, as $\psi_B = \dots$ by inverting the operator $H_B + \bar{U} + F$, and substitute for ψ_B in the first equation, we obtain (24). Similarly, ψ_B is an eigenfunction of $H_B + \bar{U} - G^B(-E)$ with the eigenvalue $E - E_S$.

One might try the approximation of replacing $H_B + \bar{U}$ in (25) by λH_B , the result being an operator diagonal in the Bloch representation:

$$G^A(F)_{k',k''} \simeq \frac{Z(\mathbf{k})}{F + \lambda H_B(\mathbf{k})} \delta_{k',k''}. \quad (26)$$

The virial theorem suggests the value -1 for the constant λ . On the other hand, for the highest energies (non-bound states) contributing to (23) the value $+1$ would presumably be the appropriate one. Therefore, it is proposed to drop this term altogether and use the approximation

$$G^A(F) \rightarrow Z/F, \quad (27)$$

in (24). That is, to approximate acceptor energy levels by the eigenvalues, E , of

$$H^A = H_A + \bar{U} - Z/(E_S - E). \quad (28)$$

On approximating the effect of the final term in (28) by first-order perturbation theory, for the ground state, we obtain (20). The condition for validity of this last approximation [not necessarily the condition for (20)

to be applicable] is presumably that $W - W(\infty)$ be small compared to $W(\infty)$. It should be noted that this derivation of (20) does not entail neglecting the chemical shift effects, but only setting $H_B + \bar{U}$ equal to zero in (25) and the application of first-order perturbation theory to (28). One might regard $W(\infty)$ and Z_0 as empirical constants to be obtained by fitting the data for $W(\epsilon)$ near the large-strain limit.

On neglecting chemical shift effects, one may apply the effective mass approximation to (28), as in (10), by expressing H_A as $H_A(-i\nabla)$ and Z as $Z(-i\nabla)$ and by reverting to $U(\mathbf{r})$ instead of \bar{U} . The binding energy as a function of strain might be obtained by minimizing the expectation of (28), with a suitable trial function, for fixed $E_S - E$ and then adding the latter to the minimum (E_{\min}) obtained, thus getting E_S for that value of $W = -E_{\min}$. In applying (28) to calculation of W for *small* strains, we would be depending on the absence of an unforeseen crossing of levels derived from the A system at large strains with those derived from the B system at large strains.¹⁸

ACKNOWLEDGMENTS

I am indebted to J. J. Hall for checking (and correcting) the computations of the results given in the Table, and for reevaluating Koenig's and his data and providing the results given in Eq. (17).

¹⁸ The acceptor ground state at zero strain is fourfold (rather than doubly) degenerate according to W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), vol. 5, p. 257. Crossing of "A" bound levels and "B" bound levels, in addition to the obvious crossing of the B bound levels with the A continuum levels, is an evident possibility; but the two lowest levels still need not cross, or meet at zero strain.