Collective Strain Splitting of Acceptor States in Silicon*

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A splitting of the ground acceptor state in silicon due to equilibrium homogeneous strains and a corresponding transition temperature have been calculated. The equilibrium homogeneous strains are due to linear terms in the strain Hamiltonian which couple the acceptor states with the strain field. The transition temperature was found to be $N_A \times 5.6 \times 10^{-20}$ °K, where N_A is the acceptor concentration in acceptors per cubic centimeter. For indium, concentrations as high as 10^{20} acceptors per cc $\mathcal{f}$ should be possible before Coulomb and exchange effects between acceptors are dominant.

I. INTRODUCTION

THE acceptor state in silicon having the lowest energy transforms like Γ_8 of the tetrahedral double group. That is, the lowest acceptor state possesses the same fourfold degeneracy as the $P_{3/2}$ valence band edge at $k=0$.[1] At temperatures sufficiently low, all holes can be considered to be in the ground acceptor state.

It has been found[2,3] that the valence band edge of silicon and germanium at $k=0$ is split under the application of a homogeneous uniaxial stress. These stresses also split the degeneracy of the ground acceptor state.[4]

If there are two acceptor states in the crystal, they should be able to interact through the strain, or phonon, field. If there are a great many acceptor states, they should collectively produce a strain in a manner analogous to the way in which a lattice of magnetic dipoles interact to produce ferromagnetism.

In this paper the lowering of the energy corresponding to this collective equilibrium strain and a corresponding transition temperature are calculated.

II. DIAGONALIZATION OF THE HAMILTONIAN

In this section a Hamiltonian density will be set up and diagonalized, yielding the energy density associated with various equilibrium strains in the crystal. The strains associated with the minimum energy density and the maximum lowering of the energy density are obtained.

Although the strain Hamiltonian for silicon doped with acceptor atoms contains strains of all wavelengths, and the equilibrium strain in the neighborhood of an acceptor state will contain strains having wavelengths comparable to the dimensions of the acceptor state and even shorter, the strains responsible for the collective effect of all acceptor states are homogeneous strains.

Therefore, in all that follows, only homogeneous strains will be considered.

If an individual acceptor is considered, it can strain in one of the normal-mode strains. However, the zero-point motion is large enough to average over all of the possible normal-mode strains and their negatives, so that on the average no strain exists. The only effect is to increase the amplitude of the zero-point motion. A homogeneous strain, however, induces a splitting even after averaging over the zero-point motions. Only the states split by the homogeneous strain are considered to be strain states of the system. This is in contrast with treatments of Jahn-Teller phase transformations of ordered impurities in which the individual atomic strain states are considered.[5]

In the strain Hamiltonian there are two types of terms. First, there are the terms independent of strain, quadratic in the strain and of higher order in the strain which are present when the acceptor concentration, and hence the hole concentration, is zero. All powers of the strain higher than the second will be neglected.

Second, there are terms which depend on the acceptor concentration. Because the acceptor concentration will always be much less than the atomic concentration of silicon, strain terms quadratic and higher in the strain which depend on acceptor concentration will be neglected. The change in elastic constants with acceptor concentration has been computed only for quite high acceptor concentrations[6] and will be neglected here. The linear terms in the Hamiltonian exist because the acceptor state is a wave packet of states taken from the top of the valence band, and exhibits the degeneracy in the valence band. The Jahn-Teller effect[7] states that, if a nonlinear symmetric arrangement of atoms has a degenerate ground state (not including spin degeneracy), there will exist in the Hamiltonian nonvanishing terms linear in the displacement of the atoms which destroy the symmetry and split the degeneracy.

The most general form for these linear terms for a crystal with cubic symmetry has been given by Kleiner

[1] W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.
[2] W. H. Kleiner and C. M. Roth, Phys. Rev. Letters **2**, 334 (1959).
[3] J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).
[4] G. Feher, J. C. Hensel, and E. A. Gere, Phys. Rev. Letters **5**, 309 (1960).

[5] P. J. Wojtowicz, Phys. Rev. **116**, 32 (1959).
[6] P. Csavinszky and N. G. Einspruch, Phys. Rev. **132**, 2435 (1963).
[7] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **161**, 220 (1937).

and Roth[2] and can be obtained from symmetry considerations alone. The values of the deformation potential coefficients D_u and D_u' for states in the valence-band edge of silicon at $k=0$ have been determined by Hensel and Feher.[3] Because the ground acceptor state has the same symmetry as the valence-band edge, the linear terms caused by the acceptor state will have exactly the same form as those for the valence-band edge, except for a change in the deformation potential coefficients.

If the binding energy of the acceptor state were much less than the energy lowering due to the equilibrium strain, the deformation potential coefficients obtained for the valence band edge by Hensel and Feher could be used for the acceptor state. Although this condition is not satisfied, these deformation potential coefficients will be used. The Hamiltonian density due to acceptor states is taken to be the acceptor concentration times the energy per hole given by Kleiner and Roth.[2]

The Hamiltonian density is then

$$\mathcal{H} = \mathcal{H}_0 + (\tfrac{1}{2}c_{11})\sum_i e_{ii}^2 + c_{12}\sum_{i>j} e_{ii}e_{jj} + (\tfrac{1}{2}c_{44})\sum_{i>j} e_{ij}^2$$
$$+ N_A\{D_d^v \sum_i e_{ii} + (\tfrac{2}{3}D_u)\sum_i (J_i^2 - \tfrac{1}{2}J^2)e_{ii}$$
$$+ (\tfrac{2}{3}D_u')\sum_{i>j} [(J_iJ_j + J_jJ_i)/2]e_{ij}\}, \quad (1)$$

where c_{ii} and c_{ij} are the elastic stiffness constants, e_{ii} and e_{ij} are the conventional strain components,[3] D_d^v, D_u, and D_u' are the deformation potential coefficients appropriate to the various types of strain, $\mathcal{H}_0$ is the Hamiltonian density with no strain, N_A is the acceptor concentration, J_i is an angular momentum matrix for angular momentum $\tfrac{3}{2}$, and the sums over i and j run from one to three over the Cartesian components. Where no angular momentum matrix is indicated, the identity matrix should be taken, because the terms independent of acceptor concentration do not split the acceptor states.

If a conventional phase for our angular momentum matrices is chosen,[8] we can write our Hamiltonian in matrix form.

$$\mathcal{H} = \begin{bmatrix} \epsilon+Q_1+Q_2 & Q_5-iQ_6 & Q_3-iQ_4 & 0 \\ Q_5+iQ_6 & \epsilon+Q_1-Q_2 & 0 & Q_3-iQ_4 \\ Q_3+iQ_4 & 0 & \epsilon+Q_1-Q_2 & -Q_5+iQ_6 \\ 0 & Q_3+iQ_4 & -Q_5-iQ_6 & \epsilon+Q_1+Q_2 \end{bmatrix}, \quad (2)$$

where

$$Q_1 = N_A D_d^v (e_{xx}+e_{yy}+e_{zz});$$
$$Q_2 = N_A(\tfrac{2}{3}D_\mu)[e_{zz} - \tfrac{1}{2}(e_{xx}+e_{yy})];$$
$$Q_3 = N_A(\tfrac{2}{3}D_u)(\tfrac{1}{2}\sqrt{3})(e_{xx}-e_{yy}); \quad (3)$$
$$Q_4 = N_A(\tfrac{2}{3}D_u')(\tfrac{1}{2}\sqrt{3})e_{xy};$$
$$Q_5 = N_A(\tfrac{2}{3}D_u')(\tfrac{1}{2}\sqrt{3})e_{xz};$$
$$Q_6 = N_A(\tfrac{2}{3}D_u')(\tfrac{1}{2}\sqrt{3})e_{yz},$$

[8] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 146.

and

$$\epsilon = E_0 + (\tfrac{1}{2}c_{11})\sum_i e_{ii}^2 + c_{12}\sum_{i>j} e_{ii}e_{jj} + (\tfrac{1}{2}c_{44})\sum_{i>j} e_{ij}^2; \quad (4)$$

or, in terms of the Q_i,

$$\epsilon = E_0 + \frac{c_{11}+2c_{12}}{6(D_d^v N_A)^2}Q_1^2 + \frac{c_{11}-c_{12}}{3(\tfrac{2}{3}N_A D_u)^2}(Q_2^2+Q_3^2)$$
$$+ \frac{2c_{44}}{3(\tfrac{2}{3}N_A D_u')^2}(Q_4^2+Q_5^2+Q_6^2). \quad (5)$$

This matrix can be diagonalized to give eigenvalues for the energy density,

$$\lambda = \epsilon + Q_1 \pm (Q_2^2+Q_3^2+Q_4^2+Q_5^2+Q_6^2)^{1/2}. \quad (6)$$

The minimum for the energy density cannot depend on the particular choice of Q_2 and Q_3 as long as $Q_2^2+Q_3^2$ is equal to a constant. The same degeneracy holds for Q_4, Q_5, and Q_6. Also, strains of the type Q_1 are separated from the other types and cause no energy splitting. Minimizing the energy density λ with respect to Q_1, one obtains an equilibrium value for Q_1. Terms in Q_1 can be included with the terms independent of strain to form the arbitrary zero of our energy.

The energy density change due to the other strains is

$$\lambda' = Ax^2 + By^2 \pm (x^2+y^2)^{1/2}, \quad (7)$$

where

$$A = \tfrac{1}{3}(c_{11}-c_{12})(\tfrac{2}{3}N_A D_u)^2; \quad B = \tfrac{1}{3}2c_{44}(\tfrac{2}{3}N_A D_u')^2; \quad (8)$$
$$x^2 = Q_2^2+Q_3^2; \qquad\qquad y^2 = Q_4^2+Q_5^2+Q_6^2.$$

The energy density can be minimized with respect to x and y by finding the values for x and y for which the first derivative of λ' with respect to both x and y is equal to zero. For $A \neq B$, as is usually the case, either x or y must be zero at equilibrium. However, $x=y=0$ gives $\lambda'=0$ and is not a minimum for λ'. If $A>B$, as is true for silicon, the minimum energy density is

$$\lambda_{\min}' = -1/4B = -N_A^2 D_u'^2/6c_{44}, \quad (9)$$

and the corresponding distortions are

$$e_{xy}^2 + e_{xz}^2 + e_{yz}^2 = N_A^2 D_u'^2/3c_{44}^2;$$
$$e_{xx} = e_{yy} = e_{zz} = Q_1/3N_A D_d^v. \quad (10)$$

The strains e_{xx}, e_{yy}, and e_{zz} are chosen so that Q_2 and Q_3 are zero, and their value is determined by the value of Q_1 at equilibrium.

III. THE WEISS FIELD METHOD

The analogy with ferromagnetism will now be pursued, letting the strain field play the part of the magnetic field, and the average value of the angular momentum components of the acceptor state play the part of the magnetization. It will be found that the ratio of the average angular momentum components

to the applied strains obeys a "Curie-Weiss law," and the transition temperature can be computed.

The response of the crystal to an applied strain must be determined. If the applied strain is of the form e_{xy}, then a "Weiss field" of the same form is assumed.

$$e_0 = e_{xy}|_0; \quad e_{xx}|_0 = e_{yy}|_0 = e_{zz}|_0 = e_{xz}|_0 = e_{yz}|_0 = 0. \quad (11)$$

The notation $|_0$ means to evaluate the strain with no external strain fields applied.

$$e_{xy} = e_0 + e_{xy}'; \quad e_{xx} = e_{xx}'; \quad \text{etc.,} \quad (12)$$

where e_{xy}' is the applied strain.

The Hamiltonian for the splitting of the acceptor state due to the total strain field e_{xy} is

$$\mathcal{3C}_S = \tfrac{2}{3} D_u'[(J_x J_y + J_y J_x)/2] e_{xy}. \quad (13)$$

After diagonalizing (13), one finds that the acceptor level is split into two states, each twofold degenerate, with an energy difference

$$\Delta E = |(2/\sqrt{3}) D_u' e_{xy}|. \quad (14)$$

For the higher energy state, the eigenfunctions are $(\psi_{1/2} + i\psi_{-3/2})/\sqrt{2}$; $(\psi_{3/2} + i\psi_{-1/2})/\sqrt{2}$. This state will be denoted by $+$. The lower energy state has eigenfunctions $(\psi_{1/2} - i\psi_{-3/2})\sqrt{2}$; $(\psi_{3/2} - i\psi_{-1/2})/\sqrt{2}$. This state will be denoted by $-$.

The density of states at each level is

$$N_+ = \frac{N_A \exp(-D_u' e_{xy}/\sqrt{3}kT)}{\exp(D_u' e_{xy}/\sqrt{3}kT) + \exp(-D_u' e_{xy}/\sqrt{3}kT)};$$

$$N_- = \frac{N_A \exp(D_u' e_{xy}/\sqrt{3}kT)}{\exp(D_u' e_{xy}/\sqrt{3}kT) + \exp(-D_u' e_{xy}/\sqrt{3}kT)}. \quad (15)$$

The density of the angular momentum coefficient is

$$\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}} = \tfrac{1}{2}\langle + | J_x J_y + J_y J_x | + \rangle N_+ \\ + \tfrac{1}{2}\langle - | J_x J_y + J_y J_x | - \rangle N_-. \quad (16)$$

Here $\langle + | | + \rangle$ indicates that the expectation value between the upper states should be taken. This gives the upper eigenvalue $+\sqrt{3}/2$.

Substituting (15) into (16), one obtains

$$\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}} = -N_A(\sqrt{3}/2) \tanh(D_u' e_{xy}/\sqrt{3}kT), \quad (17)$$

This form of strain dependence has been experimentally verified for the case of O_2 centers in alkali halides.[9] Equation (17) becomes, for $D_u' e_{xy} \ll kT$,

$$\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}} \\ = -(N_A D_u'/2k)(e_{xy}/T) = C(e_{xy}/T). \quad (18)$$

The expectation values between $+$ or $-$ states for all other angular momentum combinations in our Hamiltonian (1) vanish, so that the assumed strain gives an average value for only its coefficient.

This average splitting of the acceptor states in turn

leads to an equilibrium strain in the crystal. The energy density is

$$\mathcal{E} = \tfrac{2}{3} D_u'[\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}}] e_{xy} \\ + \tfrac{1}{2} c_{11} \sum_i e_{ii}^2 + c_{12} \sum_{i>j} e_{ii} e_{jj} \\ + \tfrac{1}{2} c_{44} \sum_{i>j} e_{ij}^2. \quad (19)$$

The energy density is then minimized with respect to the possible strains to obtain the equilibrium strains

$$e_{xx}|_0 = e_{yy}|_0 = e_{zz}|_0 = e_{xz}|_0 = e_{yz}|_0 = 0;$$

$$e_{xy}|_0 = e_0 = -\tfrac{2}{3} D_u'[\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}}] \\ = \gamma[\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}}]. \quad (20)$$

Equations (12), (18), and (20) yield

$$\frac{\tfrac{1}{2}\langle J_x J_y + J_y J_x \rangle_{\text{av}}}{e_{xy}'} = \frac{C}{T - C\gamma}. \quad (21)$$

$C\gamma$, the transition temperature, is given by

$$T_c = C\gamma = N_A D_u'^2/3kc_{44}. \quad (22)$$

Comparing (9) and (22), one obtains for the lowering of the energy density

$$\lambda_{\min}' = -\tfrac{1}{2} N_A k T_c. \quad (23)$$

The splitting of the lowest acceptor level is then

$$\Delta E = kT_c, \quad (24)$$

which might have been expected.

Using $D_u' = 2.68 \pm 0.25$ eV, determined by Hensel and Feher,[3] and a value for $c_{44} = 8.007 \times 10^{11}$ dyn/cm^2, which it has at low temperatures and which varies little with temperature at low temperatures,[6,10] one obtains

$$T_c = N_A \times 5.6 \times 10^{-20} {}^\circ\text{K} = n_A \times 2800 {}^\circ\text{K}, \quad (25)$$

where n_A is the fractional number of acceptors and N_A is the acceptor concentration in acceptors per cc.

Feher, Hensel, and Gere[4] found that a stress of about 300 kg/cm^2 in the (100) direction was necessary to split the ground acceptor state enough for paramagnetic resonance absorption transitions to be observed over the broadening due to the background of random strains in the crystal. The energy splitting due to an applied stress in the [100] direction[3] is

$$\Delta E_S = \tfrac{4}{3} D_u T/(c_{11} - c_{12}), \quad (26)$$

where T is the applied stress. The splitting necessary for transitions to be observed is roughly 8×10^{-5} eV, or 0.9°K.

In order to observe the effect of the equilibrium strain, one would like to increase the concentration to a value which would allow the energy splitting of (24) to be greater than the energy splitting necessary to overcome the random strains in the crystal. However,

[9] W. Känzig, Phys. Chem. Solids 23, 479 (1962).

[10] H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

TABLE I. Approximate concentrations and
transition temperatures.

Acceptor	N_A in acc/cc	T_c in °K
B	10^{18}	0.06
Al	3×10^{18}	0.17
Ga	4×10^{18}	0.22
In	10^{20}	5.6

at very high concentrations, the acceptor states gain more energy by binding into hydrogen-like molecules and finally bands than they gain due to the Jahn-Teller effect. The energy of binding into hydrogen-like molecules comes from both direct Coulomb and exchange interactions. For concentrations in the range of inter-

est, this binding energy is much larger than the energy due to Van der Waals forces between acceptor states and the direct magnetic coupling between acceptor states.

Therefore, one must know at what concentration the molecular binding energy exceeds the energy lowering computed from (9). Table I gives the approximate concentrations at which this occurs, and the transition temperatures associated with these concentrations.

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Band Structure of Gallium Phosphide from Optical Experiments at High Pressure[*]

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The effect of hydrostatic pressure on the following optical properties of GaP has been measured at room temperature: the fundamental absorption edge region from 2.2 to 2.7 eV, an infrared absorption band appearing in n-type material at 0.3–0.5 eV, peaks in the reflectivity spectrum at 2.8 and 3.7 eV, and recombination radiation in forward-biased p-n junctions at 1.7–2.3 eV. The results have been interpreted by means of a proposed energy band structure in which the conduction band states $X_1{}^c$, $X_3{}^c$, $\Gamma_1{}^c$, $\Gamma_{15}{}^c$ are located at energies of 2.2, 2.5, 2.8, 3.7 eV, respectively, above the valence band maximum at $\Gamma_{15}{}^v$. The following pressure coefficients have been measured (the transition involved is given in parenthesis), where energy is expressed in eV and pressure in 10^6 bars: $E_G(\Gamma_{15}{}^v \to X_1{}^c) = 2.22 - 1.1P$; $E_0(\Gamma_{15}{}^v \to \Gamma_1{}^c) = 2.78 + 10.7P$; $E_0{}'(\Gamma_{15}{}^v \to \Gamma_{15}{}^c) = 3.71 + 5.8P$; $\Delta E_2(X_1{}^c \to X_3{}^c) = 0.3 + 1P$. The coefficients of E_G and $E_0{}'$ are close to those for the corresponding transitions in Si; that of E_0 is close to the corresponding coefficient in Ge. The weak reflectivity peak at 2.8 eV, the direct gap, shifts with temperature at a rate of about -4.6×10^{-4} eV/°K, compared to a value of about -5.2×10^{-4} eV/°K for the 2.2 eV indirect gap.

1. INTRODUCTION

THIS paper describes an experimental investigation of the electronic energy band structure of GaP. The approach taken in this study was to measure the effect of hydrostatic pressure on certain optical properties in the infrared, visible, and near ultraviolet regions of the spectrum. Included in these were absorption near the fundamental absorption edge, extrinsic absorption, reflectivity, and recombination radiation. Several features of the lowest conduction bands have been elucidated in the energy range from 2 to 4 eV above the valence band maximum.

Part of the basis for this work is a systematic correlation inferred from earlier work on pressure effects in group 4 and group 3–5 semiconductors.[1–8] It has been

observed that corresponding energy separations in these materials have similar pressure coefficients. In other words, the effect of pressure on the energy of an electronic transition depends primarily on the particular type of final and initial states involved (each specified by a band index n, a reduced wave vector k, and a group-theoretic classification), and is relatively insensitive to choice of material from among this class of simple semiconductors. We have listed some pressure

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[1] Some of the principal results of this work were briefly mentioned in R. Zallen and W. Paul, Bull. Am. Phys. Soc. 9, 61 (1964).

[2] W. Paul and D. M. Warschauer, Phys. Chem. Solids 5, 89 (1958); 5, 102 (1958); 6, 6 (1958).

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[6] W. Paul and H. Brooks, Progr. Semiconductors 7, 135 (1963).

[7] R. Zallen, W. Paul, and J. Tauc, Bull. Am. Phys. Soc. 7, 185 (1962); some of these data are shown in the article by J. Tauc, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (Institute of Physics and the Physical Society, London, 1962), p. 341.

[8] R. Zallen, Gordon McKay Laboratory of Applied Science, Harvard University, Technical Report HP-12, 1964 (unpublished); R. Zallen and W. Paul, unpublished data.