Deformation Potentials and Mobilities in Non-Polar Crystals

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The method of effective mass, extended to apply to gradual shifts in energy bands resulting from deformations of the crystal lattice, is used to estimate the interaction between electrons of thermal energy and the acoustical modes of vibration. The mobilities of electrons and holes are thus related to the shifts of the conduction and valence-bond (filled) bands, respectively, associated with dilations of longitudinal waves. The theory is checked by comparison of the sum of the shifts of the conduction and valence-bond bands, as derived from the mobilities, with the shift of the energy gap with dilation. The latter is obtained independently for silicon, germanium and tellurium from one or more of the following: (1) the change in intrinsic conductivity with pressure, (2) the change in resistance of an n–p junction with pressure, and (3) the variation of intrinsic concentration with temperature and the thermal expansion coefficient. Higher mobilities of electrons and holes in germanium as compared with silicon are correlated with a smaller shift of energy gap with dilation.

I. INTRODUCTION

THE mobilities of electrons and holes in non-polar semiconductors and insulators are determined by interactions with the acoustical vibrations of the lattice as well as by scattering by impurities or other lattice defects. The former generally predominates in relatively pure materials in which the concentration of carriers is small. Classical rather than quantum statistics may then be applied to the conduction electrons and the wave-length of an electron of thermal energy is large compared with the lattice constant. Such electrons interact only with acoustical vibrational modes of comparably long wave-length whose properties are determined by the bulk elastic constants. The purpose of the present paper is to calculate the magnitude of this interaction on the assumption that local deformations produced by the lattice waves are similar to those in homogeneously deformed crystals. In particular, we shall show that for the case of non-degenerate, spherical energy surfaces in the Brillouin zone the lattice scattering is determined by shifts in the energy bands resulting from dilations associated with acoustical waves.[1]

The discussion of the motion of electrons or holes in semiconductors is usually based on the use of the concept of effective mass. If a gradually varying electrostatic potential is superimposed on the periodic potential of a crystal lattice, it is often a good approximation to neglect the periodic potential and to calculate the motion of an electron of appropriate effective mass in the gradually varying potential. Justifications for this procedure have been given by Peckar,[2] Slater,[3] and James.[4] The criterion is essentially that the change in the gradually varying potential in one period be small compared with the periodic potential. One of our principal aims is to show that this theory can be extended

to cover effective potentials which correspond to the position of the energy band boundary as affected by a gradually varying dilation. We shall call effective potentials of this sort, which can be produced by acoustical waves of long wave-length, *deformation potentials*.

The velocity, v, of an electron with energy k_0T (k_0 = Boltzmann's constant) at room temperature is about 10^7 cm/sec. The wave-length, $\lambda = h/mv$, of electron with this velocity is about 7×10^{-7} cm, which is large compared with the lattice constant. The energy of a phonon of corresponding wave-length is

$$h\nu = hc/\lambda = mvc = (c/v)mv^2, \qquad (1.1)$$

where c is the velocity of the acoustical wave. Since $c \sim 5 \times 10^5$ cm/sec. as compared with $v \sim 10^7$ cm/sec., the energy of the phonon involved in scattering is small compared with k_0T and with the energy of the conduction electrons. This implies that the pertinent acoustical waves can be treated by classical methods, even at fairly low temperatures. In this latter respect the theory for non-polar crystals is simpler than for metals or for polar compounds.

The theory of scattering by acoustical vibrational modes has been discussed by Sommerfeld and Bethe,[5] by Wilson[6] and by Seitz.[7] Making certain assumptions concerning the interaction between electrons and lattice waves, they show that (1) scattering is essentially elastic, (2) scattering is isotropic, and (3) the mean free path is independent of the velocity of the electron and is inversely proportional to the absolute temperature. The mobility then varies as $T^{-\frac{3}{2}}$, as is observed in relatively pure samples of Ge, Si, and Te.

Germanium and silicon have a diamond structure with two atoms per unit cell, so that there are two branches to the vibrational spectrum. Seitz has con-

[1] W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950).
[2] S. Peckar, J. Phys. USSR **10**, 431 (1946).
[3] J. C. Slater, Phys. Rev. **76**, 1592 (1949). Slater's proof is based on a method of G. H. Wannier, Phys. Rev. **52**, 191 (1937).
[4] H. M. James, Phys. Rev. **76**, 1602 (1949).

[5] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (1933), Vol. XXIV.
[6] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, England, 1936).
[7] F. Seitz, Phys. Rev. **73**, 549 (1948).

sidered the theory of scattering by the upper branch as well as by the acoustical branch. There is no experimental evidence that scattering by modes in the upper branch plays a role in the conductivity of non-polar semiconductors. Frohlich and Mott, on the other hand, have shown that a major cause of scattering in polar crystals is the interaction with optical modes of long wave-length. We shall be concerned only with the acoustical branch.

A calculation of the actual magnitude of the mean free path or mobility requires an evaluation of a matrix element of the interaction between electrons and lattice vibrations and some assumption regarding the form and magnitude of this interaction. While some calculations of the matrix element have been given for metals, no explicit calculations have been made previously for non-polar semiconductors. Making use of the deformation potentials, we evaluate the matrix element in terms of certain general properties of the energy band picture in a way which permits correlation with other experimental data. The details of this calculation are given in the Appendix.

The deformation potential is determined by shifts in the energy bands with dilations of the crystal produced by thermal vibrations, and is calculable from the variation in energy band boundaries with lattice constant. The calculation of energy bands has not progressed to the point where these variations can be obtained from first principles. It·is possible to check the theory from experimental data, however, because the theory predicts that quantities deduced from the mobilities will be definitely related to effects produced by pressure and by thermal expansion.

II. ENERGY BANDS IN DEFORMED CRYSTALS

In Fig. 1 we give a qualitative diagram showing how the band structure may be expected to vary with lattice constant for a crystal like silicon or germanium.[8] In these crystals a decrease in lattice constant increases the separation between the valence-bond, or filled, band and the conduction band. It should be noted that the energies of the valence-bond and conduction bands, E_v and E_c, may shift in opposite directions as a result of the varying dilation of a lattice wave, thus changing the energy gap, $E_G = E_c - E_v$. In contrast, a varying electrostatic potential, in the absence of distortion, moves the bands up and down together (cf. Fig. 1 of reference 1). We shall shortly consider the effects of more general deformations than pure compressions or dilations and in Section III we shall show how the resulting shifts can be treated as effective potentials.

We shall next consider and dispose of a difficulty in applying curves like those of Fig. 1 to obtain shifts in the energy bands in different parts of a deformed

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[8] The figure is based on calculations of the energy bands in diamond by G. E. Kimball, J. Chem. Phys. **3**, 560 (1935). The band structure for silicon has been calculated by J. F. Mullaney, Phys. Rev. **66**, 326 (1944).

crystal. This difficulty has to do with the fact that deformations may set up electrostatic potentials. When curves like those of Fig. 1 are computed numerically, some arbitrary choice of the zero of electrostatic potential must be made. For example, in calculating curves for diamond, Kimball[8] used a potential which took on the same numerical value near the interior of the atom for all lattice constants; as he points out, this choice is purely arbitrary.

Actually the potential in the interior of the atoms varies with dilation. For example, in the case of semiconductors with large scale deformations the potential is determined as follows: Start with an undeformed crystal of lattice constant a_0. Imagine a deformation which leaves one portion of the crystal unaltered, but, as a result of a continuously varying strain, produces another large region in which the crystal is uniformly dilated to a value a_1. Let the height of the Fermi level corresponding to electrical neutrality and measured relative to the potential energy of an electron at a point fixed near the interior of an atom be U for the undeformed crystal and U' for the deformed crystal. In equilibrium, the potentials will adjust themselves to bring the Fermi levels in different parts of the crystal
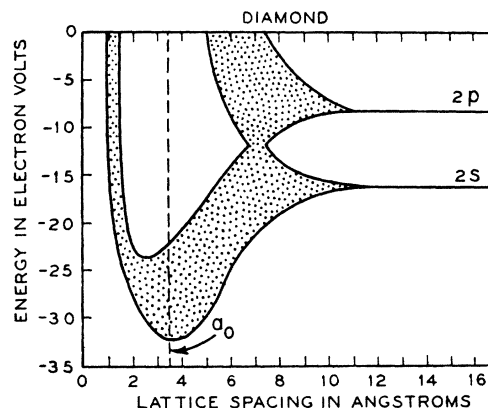

FIG. 1. Energy bands for diamond *versus* lattice spacing (see reference 8).

to the same height. This implies a difference of $U' - U$ in potential energy resulting from the change in electrostatic potential near the interior of an atom. The electrostatic potential difference is produced in part by the space charge of the carriers and fixed impurity ions and in part by polarizations due to relative displacement of the electrons and atomic nuclei in the region of varying strain. As a specific example, in a n-type semiconductor, the requirement of electrical neutrality will lead to approximately the same value of E_c in both parts of the crystal so as to produce the electron densities which compensate the impurity ions.

For the short wave-length lattice waves which contributed to scattering, however, the space charge of the carriers and impurities in the semiconductor is insufficient to set up appreciable potential differences over

the relatively short distances involved. In fact, for the wave-length of a thermal electron in germanium of resistivity of 5 ohm-cm, there will be about 10^{-5} electrons on the average in each cube one wave-length on an edge. Even for higher densities, the effect is negligible. Longitudinal lattice waves of wave vector $\mathbf{k}$ produce electrostic potentials of the order $Ne\Delta/k^2$, where N is the concentration of impurity ions and Δ is the dilation of the wave. This effect is negligible compared with the effect of shifting of the bands,[9] except for very small values of k (very long wave-lengths). In addition to the space charge of the carriers, there may be local polarizations and electric fields resulting from relative displacements of neighboring atoms; for non-polar crystals, these will also be negligible. Accordingly, we assume that electric field effects which made the electrostatic potential depend on the strain pattern are negligible for deformation waves of interest for scattering and consider the energies E_c and E_v of the conduction and valence-bond bands each to be a unique function of the local strain.

For a cubic crystal subject to a homogeneous strain ϵ_{ij}, the band energies E_c or E_v can be expressed in the form,

$$E(\epsilon_{ij}) = E_0 + E_1\Delta, \qquad (2.1)$$

where Δ is the dilation

$$\Delta = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}, \qquad (2.2)$$

since by symmetry any term containing ϵ_{ij} with $i \neq j$, which changes sign by reflection in a symmetry plane, must have a zero coefficient. The parameter E_1 has the dimensions of an energy, and we shall see that it is closely related to the interaction constant C used in previous theories of scattering.[5,6] If the energy band is degenerate, then relative displacements of the different energy sheets may be produced by shearing strains. It should be possible to extend the treatment of (2.1) and (2.2) to such cases by methods similar to those employed in determining the shape of the energy surfaces.[9a] It is probable that effects associated with complex shapes of the energy surfaces may account for magnetoresistive effects in germanium and silicon. The agreement presented in Table III between the predictions based on (2.1) and experiment suggests that the contributions of scattering due to other terms is relatively small compared to E_1. In this paper we shall neglect the possibility of degenerate energy bands and shall proceed on the basis of spherical energy surfaces in the Brillouin zone.

In a strained crystal a wave function with crystal momentum $\mathbf{P}$ [i.e., having a factor $\exp(i\mathbf{P}\cdot\mathbf{r}/\hbar)$] will have an energy

$$E(P, \epsilon_{ij}) = E_0(P) + \Sigma_{ij}\epsilon_{ij}E_{ij}(P). \qquad (2.3)$$

[9] For example, with $N \sim 10^{17}/\text{cm}^3$ and $k \sim 10^7$ cm^{-1}, Ne/k^2 is about 5×10^{-7} e.s.u. or 1.5×10^{-5} volt. This potential contributes a negligible amount compared to E_1 of Eq. (2.1).
[9a] W. Shockley, Phys. Rev. 78, 173 (1950).

For small P, E_{ij} can be expanded in the series:

$$E_{ij}(P) = E_1\delta_{ij} + \Sigma_{kl}\beta_{ijkl}P_kP_l + \cdots. \qquad (2.4)$$

Thus the energy for a state with P small is of the form

$$E(P, \epsilon_{ij}) = E_0(P) + E_1\Delta + \text{terms in } P^2 \text{ strains}. \qquad (2.5)$$

For electrons of thermal energy, the latter terms are generally small compared to $E_1\Delta$ and can be neglected. This is equivalent to neglecting the change in effective mass with strain.

III. THE DEFORMATION POTENTIAL THEOREMS

In the Appendix an analytical treatment is presented showing that the shift in the band edges, which can be written as $E_{1c}\Delta$ for electrons in the conduction band, and as $E_{1v}\Delta$ for holes in the valence-bond band, may be used as varying potentials in calculating the behaviors of electrons and holes. We shall refer to these potentials as *deformation potentials* and write

$$\delta U(r) = E_1\Delta(r), \qquad (3.1)$$

supplying the subscripts c and v as required. The first theorem, referred to as the *method of effective mass*, is analogous to the treatments of Wannier, Peckar, James, and Slater.[2-4] These earlier treatments show that in an undistorted lattice when a perturbation δU_s (s for electro*static*) produced by an electrostatic field is present, the wave function can be obtained by solving the equation

$$[(\hbar^2/2m^*)\nabla^2 + \delta U_s(\mathbf{r})]A(\mathbf{r}) = EA(\mathbf{r}), \qquad (3.2)$$

where $A(\mathbf{r})$ is an amplitude function. (If the crystal is not cubic, $(1/m^*)\nabla^2$ is replaced by $\Sigma \alpha_{ij}(\partial^2/\partial x_i\partial x_j)$ which can be reduced to a principal axis form $\partial^2/m_1\partial x_1^2 + \partial^2/m_2\partial x_2^2 + \partial^2/m_3\partial x_3^2$. We are not aware of a treatment for the case of degenerate energy bands.) The wave function $A(\mathbf{r})$ is a smoothly varying function which does not vary appreciably over the unit cell; if $\delta U_s(\mathbf{r})$ is so large that $A(\mathbf{r})$ does not satisfy this condition, the method of effective mass becomes inadequate without considerable refinement.

The complete wave function to a good approximation is

$$A(\mathbf{r})\psi_0(\mathbf{r}), \qquad (3.3)$$

where $\psi_0(\mathbf{r})$ is the wave function at the band edge and is either periodic with the period of the lattice or simply changes sign from cell to cell. This shows that, except for fluctuations within each unit cell, the probability density is distributed as for a particle of effective mass m^* moving in a potential δU_s. In the Appendix it is shown that if the crystal is deformed a similar theorem applies if a deformation potential

$$\delta U = E_1\Delta(\mathbf{r}) \qquad (3.4)$$

is added to δU_s in Eq. (3.2). The suitable modification of (3.3) is introduced in the treatment.

The second theorem shows that the deformation potential (3.4) is also suitable for use in a calculation of the matrix element for a transition from a state with crystal momentum $\mathbf{P}$ and wave function

$$\psi(\mathbf{r}, \mathbf{P}) = \exp(i\mathbf{P} \cdot \mathbf{r}/h)U(\mathbf{r}, \mathbf{P}), \qquad (3.5)$$

where $U(\mathbf{r}, \mathbf{P})$ has the periodicity of the undistorted lattice, to a state with momentum $\mathbf{P}'$. The matrix element is

$$M = \int \psi^*(\mathbf{r}, \mathbf{P}')\delta U(\mathbf{r})\psi(\mathbf{r}, \mathbf{P})dxdydz, \qquad (3.6)$$

where $\delta U(\mathbf{r})$ is $E_1\Delta(\mathbf{r})$ produced by a thermal vibration. The transition from $\mathbf{P}$ to $\mathbf{P}'$ can occur with either absorption or emission of a phonon. Combining the emission and absorption processes gives an effective matrix element for $P \rightarrow P'$

$$|M|^2 = E_1^2\langle\Delta^2\rangle_{\text{Av}} = E_1^2 k_0 T/Vc_{ii}, \qquad (3.7)$$

where V is the volume of the crystal and $\langle\Delta^2\rangle_{\text{Av}}$ is the average dilation of a longitudinal wave with an elastic constant $c_{ii} = \rho c_i{}^2$ having total energy k_0T, i.e., potential energy $= c_{ii}\langle\Delta^2\rangle_{\text{Av}}V/2 = k_0T/2$.

The value of the matrix element can be used in the scattering formula (details in Appendix) to give a mobility of

$$\mu = [(8\pi)^{\frac{1}{2}}h^4c_{ii}/3E_1^2m^{*5/2}k_0^{\frac{3}{2}}]T^{-\frac{3}{2}} \qquad (3.8)$$

or

$$\mu T^{3/2} = (3.2 \times 10^{-5})c_{ii}/E_1^2 \qquad (3.9)$$

if m^* is taken to be the free electron mass. In (3.9), μ is expressed in cm²/volt sec. and E_1 in ev.

In the next section we shall discuss experimental values of c_{ii} and in the following section the values of $|E_{1c}|$ and $|E_{1v}|$ obtained by inserting values for μ_n, μ_p, and c_{ii} into (3.9) and solving for $|E_1|$. The results so obtained are compared with the variation of the energy gap E_G, given by

$$E_G = E_{0G} + E_{1G}\Delta, \qquad (3.10)$$

where

$$E_{1G} = E_{1c} - E_{1v}. \qquad (3.11)$$

If the effect of dilation is to shift the energy bands in opposite directions,

$$|E_{1G}| = |E_{1c}| + |E_{1v}|. \qquad (3.12)$$

There are several empirical ways of determining E_{1G}, and estimates of this quantity have been made for Ge, Si, and Te. We shall show in Section V that values of $|E_{1c}|$ and $|E_{1v}|$ obtained from mobility data are in reasonable agreement with values of $|E_{1G}|$ obtained in other ways.

IV. DISCUSSION OF ELASTIC CONSTANTS

The important deformation waves are those which produce dilation by having a large component of atomic displacement parallel to the direction of propagation.

Since the waves of interest are long compared with the lattice constant, their velocities can be determined from the elastic constants. In an isotropic solid, the three possible polarizations consist of one purely longitudinal mode and two transverse modes; in a cubic crystal the same situation is true for wave propagating in the (100), (110), and (111) directions, which lie along symmetry axes. For other directions there is a slight mixing of longitudinal and transverse polarizations.

The elastic constants for diamond, germanium, and silicon are given in Table I. Values listed for germanium are from some recent measurements made at the Bell Telephone Laboratories.[10] The only value known for silicon is the compressibility from Bridgman's data[11] on the change of volume with pressure. Values of the compressibilities[12] of diamond, Si, Ge, and Te are given in Table II. Values of the elastic constants of silicon listed in Table I were estimated by assuming that they differ from those of germanium by a constant factor which was obtained from compressibility data. In an isotropic solid,

$$c_{44} = \tfrac{1}{2}(c_{11} - c_{12}). \qquad (4.1)$$

It can be seen from Table I that this relation is not well satisfied for these elements. Nevertheless, the velocities of longitudinal waves in the various directions are not very different.

Values of c_{ii} for different directions of propagation can be expressed directly in terms of the cubic elastic constants as shown below:

$$
\begin{array}{lll}
(100) & c_{ii} = c_{11}, & \\
(110) & c_{ii} = \tfrac{1}{2}(c_{11} + c_{12} + 2c_{44}), & (4.2) \\
(111) & c_{ii} = \tfrac{1}{3}(c_{11} + 2c_{12} + 4c_{44}). &
\end{array}
$$

For other directions of propagation, the velocities lie between the extremes at (100) and (111), and the waves are not to be strictly longitudinal. However, as can be seen from Table I, differences in c_{ii} in different directions are not large, so that the approximation we have made of treating the material as isotropic will introduce relatively small errors.

V. CALCULATION OF $|E_{1c}|$ AND $|E_{1v}|$ FROM MOBILITY DATA

Data used for the calculation of $|E_{1c}|$ and $|E_{1v}|$ from Eq. (3.9) are listed in Table III which is reproduced with some minor changes from reference 1. Although tellurium is anisotropic, it has been included for purposes of comparison, along with the elements of the fourth group which have the diamond structure. The anisotropy has been neglected. Somewhat arbitrarily we have used the value of c_{ii} in the (110) direction for elements with the diamond structure in place of the

[10] Elastic constants of germanium have been measured by McSkimin, Mason and Bond on a single crystal sample prepared by K. M. Olson.

[11] P. W. Bridgman, Proc. Am. Acad. **76**, 187 (1949).

[12] The value for diamond was computed from the elastic constants; values for Si, Ge, and Te are from Bridgman, reference 11.

TABLE I. Elastic constants (units c.g.s.$\times 10^{12}$).

	Diamond	Silicon	Germanium
c_{11}	9.3	(1.67)	1.29
c_{12}	4.1	(0.62)	0.48
c_{44}	4.15	(0.87)	0.67
c_{ii}, (100)	9.3	(1.67)	1.29
c_{ii}, (110)	10.8	(2.0)	1.55
c_{ii}, (111)	11.4	(2.1)	1.64

TABLE II. Compressibilities.

Diamond	0.17×10^{-12} c.g.s
Si	0.98
Ge	1.26
Te	4.0

appropriate average over all directions of propagation. For tellurium, we have assumed simply that c_{ii} is inversely proportional to the compressibility, and have estimated the value by comparison with diamond and Ge. Values of the mobility in silicon are from the Hall effect measurements of Pearson and Bardeen,[13] in germanium from the drift velocity measurements of Haynes,[14] and in tellurium from Johnson.[15] The mobility of electrons in diamond has been determined by Klick and Maurer[16] but the mobility of holes is unknown. From studies of bombardment induced conductivity, McKay[17] has concluded that the mobility of holes must be greater than 200 cm²/volt-sec. at room temperature. Values of $|E_{1c}|$ and $|E_{1v}|$ as determined from Eq. (3.9) are listed in the sixth and seventh rows of the table.

Equation (3.9) is based on the assumption that the effective mass is equal to the ordinary electron mass. As the mobility varies as $m_e^{-5/2}$, values of E_{1c} and E_{1v} should be multiplied by $(m/m_e)^{5/4}$ if the effective mass, m_e, differs from the ordinary mass. In the case of silicon, there is evidence that m/m_e is appropximately equal to unity for holes and is greater than unity, perhaps about 1.5, for electrons.[13] Use of the latter value would increase $|E_{1c}|$ from 6.5 to 10.7, and $|E_{1c}|+|E_{1v}|$ from 17.8 to 22. It also would increase the value of $|E_{1G}|$ estimated from concentration data (Section VI) from 33 to 40 ev, in closer agreement with the value deduced from optical data, Values of m/m_e for the other elements listed are uncertain, but are probably not far from unity.

If the conduction and valence-bond bands move in opposite directions with dilation, the magnitude of the shift in energy gap with dilation, $|E_{1G}|$, is given by the sum of $|E_{1c}|$ and $|E_{1v}|$, while if they move the same way, $|E_{1G}|$ is equal to the difference. Estimates of E_{1G} from other data (Section VI), given in the last row of

[13] G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).
[14] Pearson, Haynes, and Shockley, Phys. Rev. 78, 295 (1950).
[15] V. A. Johnson, Phys. Rev. 74, 1255 (1948).
[16] C. G. Klick and R. J. Maurer, Phys. Rev. 76, 179 (1949).
[17] Estimated by K. G. McKay from experiments on bombardment induced conductivity in diamond.

TABLE III. Derivation of shift of energy bands with dilation from mobility data and comparison with shift of energy gap with dilation.

	Diamond	Silicon	Germanium	Tellurium
(1) $c_{ii} \times 10^{-12}$ c.g.s., (110)	10.8	2.0	1.55	0.50
(2) μ_n (electrons) (295°K)	900	300	3500	530
(3) μ_p (holes) (295°K)	>200	100	1700	530
(4) $\mu_n T^{\frac{3}{2}}$	45×10^5	15×10^5	180×10^5	27×10^5
(5) $\mu_p T^{\frac{3}{2}}$	$>10 \times 10^5$	5×10^5	86×10^5	27×10^5
(6) $|E_{1c}|$ (ev)	8.8	6.5	1.7	2.4
(7) $|E_{1v}|$ (ev)	<30	11.3	2.4	2.4
(8) $|E_{1c}|+|E_{1v}|$ (ev)	<39	17.8	4.1	4.8
(9) E_{1G}(ev)	?	~ -30	~ -5	+4.0

the table, are approximately equal to the sum of $|E_{1c}|$ and $|E_{1v}|$, indicating that the former picture is correct.

The agreement between $|E_{1G}|$ and the sum of $|E_{1c}|$ and $|E_{1v}|$ is good in the cases of germanium and tellurium, and is not as good for silicon. As is discussed in the following section, the value of $|E_{1G}|$ for silicon is obtained by an indirect method which may not be reliable. In any case, *the high mobilities of electrons and holes in germanium as compared with silicon is correlated with a smaller shift in energy gap with dilation.*

VI. SHIFT OF ENERGY GAP WITH DILATION

There are two general methods for obtaining information about energy gaps in semiconductors. One is based on the long wave limit of the fundamental absorption band, and the other on the equilibrium concentrations of electrons and holes, particularly in the intrinsic temperature range.

Absorption of a light quantum in the fundamental band raises an electron from a state in the valence-bond band to a state in the conduction band. One may measure either the absorption coefficient or the photo-conductivity (or photo-voltaic effect) of the electrons and holes created by the light as a function of wave-length. At the long wave-length limit the quantum energy is assumed to be equal to the energy gap. Actually, because of thermal fluctuations and possibly also because of local irregularities, the long wave limit is not sharply defined and there is considerable uncertainty in the estimation of the energy gap. If the transition corresponding to E_G is forbidden by selection rules, the long wave limit will correspond to a larger energy than E_G.

Goucher and Briggs[18] have observed the photo-current produced by light absorbed in a p-n junction in silicon as a function of wave-length at different temperatures. They found a change in the long wave limit which corresponds to a shift in energy gap from 1.1 to 1.0 ev

[18] F. S. Goucher and H. B. Briggs (unpublished).

between liquid N_2 and room temperature, a difference of about 220°C. This corresponds to a shift of about 4.5×10^{-4} ev/°C. Becker and Fan[19] found a shift of about the same rate from measurements of the absorption coefficient between 77°K and 663°K.

If it is assumed that the temperature variation is entirely due to thermal expansion, the shift of the energy gap with dilation can be obtained by dividing the temperature coefficient by the volume coefficient of expansion. The latter is about 9×10^{-6}/°C for silicon, so that

$$E_{1G} = V dE_G/dV \sim -50 \text{ ev/unit dilation.} \quad (6.1)$$

Similar measurements of Goucher and Briggs[18] on the spectral distribution of the photo-current from an $n-p$ junction in germanium and of Briggs[20] on the absorption coefficient as a function of temperature indicate that the temperature coefficient of E_G is about the same for germanium as for silicon. As the expansion coefficient is about twice that for silicon, the optical data give a value of about -25 ev for E_{1G} for germanium.

As we shall see, methods based on the concentrations of carriers give values of E_{1G} which are smaller than those deduced above from optical data, particularly for the case of germanium; although the values obtained for the energy gaps, E_{0G}, are in reasonable agreement. The source of this discrepancy is not known.[20a] It is believed that values based on concentration data are more reliable because there is less uncertainty in the theoretical interpretation.

In the following paragraphs we shall give the theory of the relationship between concentrations and energy gap and discuss the methods which can be used to determine the energy gap and its variation with volume.

Statistical theory indicates that at any temperature and regardless of impurity concentration as long as the concentrations of carriers are so small that classical statistics may be used, the product of the electron and hole concentrations, np, is[21]

$$np = 4(2\pi mkT/h^2)^3 (m_n m_p/m^2)^{\frac{3}{2}} \exp(-E_G/kT)$$
$$= 2.4 \times 10^{31} T^3 (m_n m_p/m^2)^{\frac{3}{2}} \exp(-E_G/kT), \quad (6.2)$$

where m_n and m_p are the effective masses of the electrons and holes, respectively, and the other symbols have their usual meanings. This relation can be used in several ways to estimate E_G and its change with dilation. These are outlined below.

(A) *The variation in intrinsic conductivity with pressure.*—In the intrinsic temperature range, the concen-

trations of electrons and holes are equal and

$$n_i = p_i = 5 \times 10^{15} T^{\frac{3}{2}} (m_n m_p/m^2)^{\frac{3}{4}} \exp(-E_G/2kT). \quad (6.3)$$

The intrinsic conductivity, being proportional to $n_i \mu \propto n_i T^{-\frac{3}{2}}$ varies as

$$\sigma = \sigma_\infty \exp(-E_G/2kT). \quad (6.4)$$

The energy gap can be estimated from two conductivity measurements σ_1 and σ_2, made at temperatures, T_1 and T_2:

$$E_G = 2k \ln(\sigma_2/\sigma_1)(T_1^{-1} - T_2^{-1}). \quad (6.5)$$

This equation has been applied to Bridgman's measurements of the pressure change of resistance of tellurium to estimate the energy gap at different pressures.[22] By combining these results with data on the compressibility of Te, the change in energy gap with dilation can be determined. This gives the value $E_{1G} = 4.0$ ev listed in the last row of Table III.

If it is assumed, as is approximately the case for Te, that σ_∞ is relatively independent of pressure and that most of the change in σ comes from the change in E_G, Eq. (6.4) gives

$$dE_G/dP = -2kTd \ln(\sigma/dP). \quad (6.6)$$

The value obtained in this way can be combined with compressibility data to estimate E_{1G}.

A modification of this method has been used by Miller and Taylor,[23] who find $E_{1G} \sim -5.0$ ev for germanium.

(B) *The change of resistance of an $n-p$ junction with pressure.*—According to the theory developed by one of the authors,[24] the current flowing across an $n-p$ junction consists of a current of holes, I_p, flowing from the n-region to the p-region and a current of electrons, I_n, flowing from the p-region to the n-region. These currents are proportional, respectively, to the equilibrium concentration of holes in the n-region, p_n, and the concentration of electrons in the p-region, n_p. The net current per unit area flowing at an applied voltage V is:

$$I = I_p + I_n = e\left[\frac{D_p p_n}{L_p} + \frac{D_n n_p}{L_n}\right][\exp(eV/k_0 T) - 1], \quad (6.7)$$

where D_p and D_n are the diffusion constants for electrons and holes, respectively, and L_p and L_n are the diffusion lengths $(D_p \tau_p)^{\frac{1}{2}}$ and $(D_n \tau_n)^{\frac{1}{2}}$, and τ_p and τ_n are the mean lifetimes for holes and electrons in the n and p regions respectively.

The equilibrium concentrations of holes in the p-region, p_p, and of electrons in the n-region, n_n, are approximately constant, independent of temperature, in germanium in the neighborhood of room temperature. It follows from Eq. (6.2) that p_n and n_p each vary as

[19] M. Becker and H. Y. Fan, Phys. Rev. **76**, 1531 (1949).
[20] H. B. Briggs (unpublished).
[20a] *Note added in proof:*—T. Muto and S. Oyama (to appear in Prog. Theor. Phys.) and H. Y. Fan [Phys. Rev. **78**, 808 (1950)] have shown that a temperature shift of the energy gap can arise from interaction of electrons with lattice vibrations.
[21] See, for example, R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), second edition, Chapter 11. Equation (6.2) follows from expressions for n and p in terms of the Fermi level.

[22] J. Bardeen, Phys. Rev. **75**, 1777 (1949).
[23] P. H. Miller and J. Taylor, Phys. Rev. **76**, 179 (1949) and personal communication from Dr. Miller.
[24] W. Shockley, Bell. Sys. Tech. J. **28**, 435 (1949).

$\exp(-E_G/kT)$, and thus also

$$I \sim \exp(-E_G/kT) \tag{6.8}$$

provided that the effects of pressure on D_p, L_p, D_n, and L_n are negligible. In germanium, E_G increases with decrease in volume, so that a decrease in I and a corresponding increase in resistance with increase in pressure are to be expected.

Measurements have been made by Hall[25] at pressures up to 10,000 p.s.i. on a germanium n–p junction formed by α-particle bombardment and by Pearson[26] on a junction similarly formed and also on one formed by joining together samples of germanium of different compositions. Pearson's measurements extend to about 2000 p.s.i. Both observers found the expected increase in resistance with pressure. The interpretation of the data are complicated by the fact the current does not vary exactly with the applied voltage as is indicated by the theoretical relation (6.7). Such departures from simple theory are often found in rectifying junctions and are usually explained by a non-uniform barrier.[26a] Pearson's data give change of resistance of about 1.75 percent for 1000 p.s.i. for the deuteron junction and 1.25 percent for 1000 p.s.i. for the chemical junction. Hall's data give a change of about 1.3 percent for 1000 p.s.i. at pressures up to 10,000 p.s.i.

In order to estimate E_{1G} we have taken a resistance change of 1.4 percent per 1000 p.s.i., the average of the above measurements. The dilation corresponding to 1000 p.s.i. is about 7×10^{-5}. Thus

$$d(E_G/kT)/d \ln V = 0.014/(7 \times 10^{-5}) = -200 \tag{6.9}$$

and

$$E_{1G} = 200kT \doteq -5.0 \text{ ev.} \tag{6.10}$$

This value is about the same as that found by Miller and Taylor.[23]

(C) The variation of concentration with temperature.—The equilibrium concentrations of electrons and holes can be determined from Hall and resistivity measurements in the intrinsic range. It is found that the product of the concentrations fits a law of the form of Eq. (6.2) for both germanium and silicon, but the numerical factors are larger than the theoretical values. Neglecting differences in the effective mass from the ordinary electronic mass, the discrepancy is a factor of about 32.5 for silicon.[13] This has been explained as resulting from a change in the energy gap with temperature. If a linear variation is assumed,

$$E_G(T) = E_G(0) - \beta T. \tag{6.11}$$

A value of

$$\beta = k \ln 32.5 = 3 \times 10^{-4} \text{ ev/degree} \tag{6.12}$$

accounts for the factor 32.5. The shift in the energy gap with dilation can be obtained if it is assumed that the change with temperature is due entirely to thermal expansion. The volume coefficient of expansion of silicon is about 9×10^{-6} in the intrinsic temperature range, $\sim 500°C$. Thus

$$E_{1G} = 3 \times 10^{-4}/9 \times 10^{-6} = 33 \text{ ev.} \tag{6.13}$$

The most recent data[27] on the intrinsic conductivity of germanium give

$$np = 8.5 \times 10^{31} T^3 \exp(-8700/T), \tag{6.14}$$

so that the discrepancy from the theoretical formula is a factor of about 3.5. This gives

$$\beta = k \ln 3.5 = 10^{-4} \text{ ev/degree.} \tag{6.15}$$

The volume coefficient of expansion of germanium[9a] is about 19×10^{-6} in the temperature range of interest (20 to 200°C), so that

$$E_{1G} = 10^{-4}/19 \times 10^{-6} = 5.25 \text{ ev,} \tag{6.16}$$

in good agreement with the values obtained by the more direct methods.

It is believed that the value for tellurium is most reliable, that for germanium next, and the value for silicon the least. The uncertainty in the case of silicon is due to the fact that there are no direct measurements involving a change of properties with pressure.

In conclusion it may be pointed out that magneto-resistance experiments furnish strong evidence that the energy bands and scattering are far from isotropic in germanium. The anisotropy in scattering which arises from the anistropy in the elastic constants is insufficient to account for these results. It is possible that the bands are degenerate and so are not as simple as those assumed here. However, it seems likely that refinements of this sort will not alter the semiquantitative verification of the consequences of the energy band theory presented above.

APPENDIX: METHOD OF EFFECTIVE MASS AND CALCULATION OF ELECTRON-LATTICE INTERACTION

A. Method of Effective Mass

In this section we show that the effective mass concept may be applied to gradual changes in band structure resulting from lattice distortions, as well as to a gradually varying electrostatic potential. We follow the method of Peckar.[2] The more rigorous theory of James,[4] which is based on a one-dimensional model, can be extended in a similar manner. We have not attempted to use the methods of Wannier and Slater.[5]

An arbitrary distortion can be expressed in terms of a displacement, $\delta R(r)$, which is a function of the position vector, r. It is assumed that δR is a smoothly varying function so chosen that the displacement of the atom centered at the lattice position r_n is:

$$\delta R_n = \delta R(r_n). \tag{A.1}$$

[25] H. H. Hall (unpublished).

[26] G. L. Pearson (unpublished).

[26a] *Note added in proof:*—Hall has since made measurements on a junction, prepared by Pearson, which follows the theoretical relation. The relative change of resistance with pressure is in agreement with the earlier measurements quoted above (1.3 percent for 1000 p.s.i.).

[27] From measurements of the intrinsic conductivity of germanium made at Purdue University and at the Bell Telephone Laboratories combined with mobility values of J. R. Haynes quoted.

It is further assumed that the lattice potential in the distorted crystal depends only on the local displacement and strain. Thus if $U_0(\mathbf{r})$ is the periodic potential in the undeformed crystal and U_d is the potential in a crystal subject to the deformation δR, we take

$$U_d(\mathbf{r}) = U_0(\mathbf{r} - \delta \mathbf{R}) + U_1(\mathbf{r}, \epsilon_{ij}), \qquad \text{(A.2)}$$

where U_1 depends on the strain components

$$\epsilon_{ij} = \tfrac{1}{2}[\partial(\delta R_j)/\partial x_i + \partial(\delta R_i)/\partial x_j] \qquad \text{(A.3)}$$

and on position. For small strains, U_1 varies linearly with strain.

The wave equation for an electron in the deformed crystal may be written:

$$[(\hbar^2/2m)\nabla^2 + E - U_0(\mathbf{r} - \delta \mathbf{R}) - U_1(\mathbf{r}, \epsilon)]\psi_d(\mathbf{r}) = 0. \qquad \text{(A.4)}$$

Both δR and ϵ are assumed to be slowly varying functions of position. We shall obtain an approximate solution for ψ_d in terms of exact wave functions for electrons in a crystal subject to a homogeneous strain.

If the strain ϵ is homogeneous so that δR is a linear function of position, the wave equation for an electron with crystal momentum $\mathbf{P}$ is:

$$[(\hbar^2/2m)\nabla^2 + E_h(\mathbf{P}, \epsilon) - U_0(\mathbf{r} - \delta \mathbf{R}) - U_1(\mathbf{r}, \epsilon)]\psi_h(\mathbf{r}, \epsilon, \mathbf{P}) = 0, \quad \text{(A.5)}$$

where E_h (h for *homogeneous*, not for *hole*) is of the form of Eq. (2.3).

$$E_h(\mathbf{P}, \epsilon) = E_{h0}(\epsilon) + \Sigma_{i,j}\, \alpha_{ij}(\epsilon)P_iP_j, \qquad \text{(A.6)}$$

and where E_{h0} depends only on the dilation Δ,

$$E_{h0}(\epsilon) = E_0 + E_1\Delta. \qquad \text{(A.7)}$$

The coefficients α_{ij} depend on the effective mass in the deformed crystal. The wave function ψ_h is of the form:

$$\psi_h(\mathbf{r}, \epsilon, \mathbf{P}) = \exp(i\mathbf{P}\cdot\mathbf{r}/\hbar)u_h(\mathbf{r} - \delta \mathbf{R}, \epsilon, \mathbf{P}). \qquad \text{(A.8)}$$

When $\mathbf{P}$ is small compared to the size of the Brillouin zone, u_h can be expanded in a series of which the first two terms are:

$$u_h(\mathbf{r} - \delta \mathbf{R}, \epsilon, \mathbf{P}) = u_{h0}(\mathbf{r} - \delta \mathbf{R}, \epsilon) + i\mathbf{P}\cdot\mathbf{u}_{h1}(\mathbf{r} - \delta \mathbf{R}, \epsilon) + \cdots. \qquad \text{(A.9)}$$

Following the line of argument used by Peckar, we show that an approximate expression for ψ_d can be obtained by use of the effective mass concept. The wave equation to be used in the method of effective mass is:

$$[\hbar^2 \Sigma\, \alpha_{ij}\partial^2/(\partial x_i\partial x_j) + E - E_{h0}(\epsilon)]A(\mathbf{r}) = 0. \qquad \text{(A.10)}$$

This equation applies to an electron with effective mass given by the tensor α_{ij} moving in an effective potential, $E_{h0}(\epsilon)$, called the deformation potential, where ϵ depends on position. Suppose that a solution of this equation is expressed in the form of a Fourier series or integral:

$$A(\mathbf{r}) = \Sigma_P\, a(\mathbf{P}) \exp(i\mathbf{P}\cdot\mathbf{r}/\hbar). \qquad \text{(A.11)}$$

Substitution in (A.10) gives:

$$\Sigma\, a(\mathbf{P})[\Sigma\, \alpha_{ij}P_iP_j + E - E_{h0}(\epsilon)] \exp(i\mathbf{P}\cdot\mathbf{r}/\hbar) = 0. \qquad \text{(A.12)}$$

We shall show that

$$\psi_d = \Sigma_P\, a(\mathbf{P})\psi(\mathbf{r}, \epsilon, \mathbf{P}), \qquad \text{(A.13)}$$

with ϵ now considered to be a function of $\mathbf{r}$, is an approximate solution of (A.4) provided that ϵ varies sufficiently slowly with $\mathbf{r}$.

Substitution of (A.13) into (A.4) gives

$$\Sigma_P\, a(\mathbf{P})[E - E_{h0} - \Sigma_{i,j}\, \alpha_{ij}P_iP_j]\psi_h(\mathbf{r}, \epsilon, \mathbf{P})$$
$$= (\hbar^2/2m)\, \Sigma_P\, a(\mathbf{P}) \exp(i\mathbf{P}\cdot\mathbf{r}/\hbar)$$
$$\left[\Sigma_{j,k,l}\left\{\frac{\partial u_h}{\partial \epsilon_{kl}}\left(\frac{2iP_j}{\hbar}\frac{\partial \epsilon_{kl}}{\partial x_j} + \frac{\partial^2 \epsilon_{kl}}{\partial x_j{}^2}\right)\right.\right.$$
$$\left.\left. + 2\frac{\partial^2 u_h}{\partial \epsilon_{kl}\partial x_j}\frac{\partial \epsilon_{kl}}{\partial x_j}\right\} + \Sigma_{kl}\frac{\partial u_h}{\partial x_l}\frac{2\epsilon_{kl}}{\partial x_k}\right]. \qquad \text{(A.14)}$$

Terms quadratic in ϵ have been omitted. Use has been made of the fact that ψ_h with ϵ constant satisfied (A.5.) The terms on the right-hand side arise from terms in the kinetic energy which depend on a variation of ϵ with position and are small if this variation is sufficiently gradual. The wave function on the left-

hand side may be expanded in a power series in P to give:

$$\Sigma_P\, a(\mathbf{P})[E - E_{h0} - \Sigma_{ij}\, \alpha_{ij}P_iP_j] \exp(i\mathbf{P}\cdot\mathbf{r}/\hbar)$$
$$\times [u_{h0}(\mathbf{r}, \epsilon) + i\mathbf{P}\cdot\mathbf{u}_{h1}(\mathbf{r}, \epsilon)\cdots]. \qquad \text{(A.15)}$$

The dominant term vanishes because of (A.12). Thus (A.13) is an approximate solution of (A.4).

Peckar considers the limits of validity of the method as applied to a space variation of potential. Similar considerations apply when the shifts in the energy bands result from lattice deformations.

B. Calculation of the Matrix Element

A calculation of the probability that an electron be scattered from momentum state $\mathbf{P}'$ to state $\mathbf{P}$ as a result of an interaction with a lattice wave depends on an evaluation of the matrix element.

$$M(\mathbf{P}, \Delta') = \int \psi(\mathbf{P}')^*V_p\psi(\mathbf{P})d\tau, \qquad \text{(A.16)}$$

where V_p represents the perturbation produced by the lattice wave. The matrix element vanishes unless

$$\mathbf{P}' = \mathbf{P} \pm \hbar\mathbf{k} \pm \hbar\mathbf{K}, \qquad \text{(A.17)}$$

where $\mathbf{k}(|k| = 2\pi/\lambda)$ is the wave vector of the lattice wave and $\mathbf{K}$ is a lattice vector of the reciprocal lattice space. Since we are concerned with transitions for which both $\mathbf{P}$ and $\mathbf{P}'$ are relatively small, we can set $\mathbf{K} = 0$.

We shall show that the matrix element may be calculated by replacing V_p by the deformation potential, $E_1\Delta(\mathbf{r})$, so that

$$M(\mathbf{P}, \mathbf{P}') = \int \psi(\mathbf{P}')^*E_1\Delta(\mathbf{r})\psi(\mathbf{P})d\tau$$
$$= (E_1/V)\int \exp(\pm i\mathbf{P}\cdot\mathbf{r}/\hbar)\Delta(\mathbf{r})d\tau. \qquad \text{(A.18)}$$

where V is the volume of the crystal. Although this result follows from the method of effective mass, we shall give a direct proof of (A.18) which shows more directly the relation between the present and previous interaction potentials. It is based on the assumption that V_p is the difference between the potential in the deformed lattice, $U_d(\mathbf{r})$, as given by (A.2) and $U_0(\mathbf{r})$, the periodic potential in the undeformed lattice:

$$V_p = U_d(\mathbf{r}) - U_0(\mathbf{r}) = U_0(\mathbf{r} - \delta \mathbf{R}) - U_0(\mathbf{r}) + U_1(\mathbf{r}, \epsilon_{ij}). \qquad \text{(A.19)}$$

The first two terms on the right give the "deformable potential" used by Bloch and Bethe.[5]

We shall show that the error involved in using $E_1\Delta(\mathbf{r})$ in place of V_p is the order of $(P^2/2m) \times strains$, which is generally negligible.

The unperturbed wave functions $\psi(\mathbf{P})$ satisfy the wave equation:

$$H_0\psi(\mathbf{P}) = [-(\hbar^2/2m)\nabla^2 + U_0(\mathbf{r})]\psi(\mathbf{P}) = E_0(\mathbf{P})\psi(\mathbf{P}), \qquad \text{(A.20)}$$

where the energy,

$$E_0(\mathbf{P}) = E_0(0) + P^2/2m_e \qquad \text{(A.21)}$$

and m_e is the effective mass. The Hamiltonian for the perturbed wave function is $H_0 + V_p$.

The proof of the desired theorem is based on use of the wave functions $\psi_h(\mathbf{r}, \epsilon, \mathbf{P})$ for electrons in homogeneously strained crystals as defined by Eq. (A.8) and the related functions obtained by assuming that the strain ϵ is a slowly varying function of $\mathbf{r}$. We shall neglect terms which are quadratic in ϵ. We may write

$$\psi_h(\mathbf{r}, \epsilon, \mathbf{P}) = \psi(\mathbf{r}, \mathbf{P}) + \delta\psi(\mathbf{r}, \epsilon, \mathbf{P}), \qquad \text{(A.22)}$$

where $\delta\psi$ is of order ϵ.

To prove (A.18), first consider the integral:

$$I = \int \psi(\mathbf{r}, \mathbf{P}')[H_0 + V_p]\psi_h(\mathbf{r}, \epsilon(\mathbf{r}), \mathbf{P})d\tau. \qquad \text{(A.23)}$$

The result of the operation on ψ_h is

$$I = \int \psi(\mathbf{r}, \mathbf{P}')E_h(\mathbf{P}, \epsilon(\mathbf{r}))\psi_h(\mathbf{r}, \epsilon, \mathbf{P})d\tau$$
$$+ \text{integrals involving } \partial_h/\partial\epsilon \cdot \partial\epsilon/\partial X.$$

The latter terms, which are similar to those on the right-hand side of Eq. (A.14), are of the order of $[P^2/2m] \times strains$, and may be neglected. To terms of the same order,

$$E_h(\mathbf{P}, \epsilon) = E_0(\mathbf{P}) + E_1\Delta. \qquad (A.24)$$

Thus, omitting terms quadratic in the strain, the integral is approximately:

$$I = \int \psi(\mathbf{P'})^* E_1\Delta\psi(\mathbf{P})d\epsilon + E_0(\mathbf{P})\int \psi(\mathbf{P'})^*\delta\psi(\mathbf{P})d\tau. \qquad (A.25)$$

We now evaluate I again by expanding the last two terms of Eq. (A.23) and using the fact that $\psi(\mathbf{P})$ and $\psi(\mathbf{P'})$ are orthogonal eigenfunctions of H_0. This gives

$$I = \int \psi(\mathbf{P'})^* V_p\psi(\mathbf{P})d\tau + \int \psi(\mathbf{P'})^* H_0\psi(\mathbf{P})d\tau$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (A.26)$$
$$= \int \psi(\mathbf{P'})^* V_p\psi(\mathbf{P})d\tau + E_0(\mathbf{P'})\int \psi(\mathbf{P'})\delta\psi(\mathbf{P})d\tau.$$

The second step involves the Hermitian character of H_0. Solving (A.25) and (A.26) for the desired integral gives

$$\int \psi(\mathbf{P'})^* V_p\psi(\mathbf{P})d\tau = \int \psi(\mathbf{P'})^* E_1\Delta\psi(\mathbf{P})d\tau$$
$$+ [E_0(\mathbf{P}) - E_0(\mathbf{P'})]\int \psi(\mathbf{P'})^*\delta\psi(\mathbf{P})d\tau. \qquad (A.27)$$

The last term is the order $P^2/2m \times strains$ and can be neglected. Thus we have shown that to terms of this order V_p can be replaced by the deformation potential $E_1\Delta(\mathbf{r})$ in computing the matrix element.

With use of $E_1\Delta$ for V_p, the evaluation of the matrix element is relatively simple. The displacement of an atom at $\mathbf{R}_n$ resulting from a lattice wave of wave vector $\mathbf{k}$ is

$$\delta\mathbf{R}(\mathbf{R}_n) = N^{-\frac{1}{2}}\mathbf{l}_k(a_k \exp(i\mathbf{k}\cdot\mathbf{R}_n) + a_k^* \exp(-i\mathbf{k}\cdot\mathbf{R}_n)), \qquad (A.28)$$

where $\mathbf{l}_k$ is a unit vector in the direction of the displacement and N is the number of atoms in unit volume. At high temperatures, when the lattice waves are fully excited, the amplitude of the wave is given by

$$|a_k|^2 = k_0T/2Mk^2c_l^2, \qquad (A.29)$$

where k_0 is Boltzmann's constant, M is the mass of an atom and c_l is the velocity of a longitudinal wave. The dilation resulting from $\delta\mathbf{R}$ for a wave of long wave-length is

$$\Delta(\mathbf{r}) = \mathrm{div}\,\delta\mathbf{R}(\mathbf{r})$$
$$= iN^{-\frac{1}{2}}(\mathbf{k}\cdot\mathbf{l}_k)[a_k \exp(i\mathbf{k}\cdot\mathbf{r}) - a_k^* \exp(-i\mathbf{k}\cdot\mathbf{r})]. \qquad (A.30)$$

Only the longitudinal component of the wave contributes to the dilation and thus to the scattering of electrons.

When (A.30) is inserted into (A.18) it is found that the integral vanishes unless the selection rule (A.17) is satisfied, in which case

$$M(\mathbf{P}, \mathbf{P'}) = iN^{-\frac{1}{2}}(\mathbf{k}\cdot\mathbf{l}_k)a_k E_1\int u_0(\mathbf{r}, \mathbf{P'})^* u_0(r, \mathbf{P})d\tau. \qquad (A.31)$$

Since

$$u_0(\mathbf{r}, \mathbf{P}) = u_0(\mathbf{r}) + \Sigma P_k u_k(\mathbf{r}) + \cdots \qquad (A.32)$$

and $U_0(\mathbf{r})$ is normalized, the integral is unity to terms of the order P^2. Thus for longitudinal waves,

$$|M(\mathbf{P}, \mathbf{P'})|^2 = N^{-1}E_1^2k^2a_k^2. \qquad (A.33)$$

The same result is obtained after summing over the three directions of motion in case the waves are not strictly longitudinal and transverse. Inserting (A.29) for a_k^2, we find:

$$|M(\mathbf{P}, \mathbf{P'})|^2 = E_1^2k_0T/2NMc_l^2 = E_1^2k_0T/2\rho c_l^2, \qquad (A.34)$$

where $\rho = NM$ is the density. It should be noted that $|M(\mathbf{P}, \mathbf{P'})|^2$ is independent of $\mathbf{P}$ and $\mathbf{P'}$ if it is assumed that c_l is independent of the direction of propagation of the acoustic wave.

We can replace ρc_l^2 by the elastic constant c_{ii} for longitudinal strain in the direction of propagation of the wave,

$$c_{ii} = \rho c_l^2. \qquad (A.35)$$

It should be noted that interaction constant C used by Sommerfeld and Bethe[5] and by Seitz[7] is equal to $(3/2)E_1$; that used by Wilson[6] is equal to E_1.

The reciprocal of the relaxation time for an electron of momentum $\mathbf{P}$ is:

$$1/\tau = (m_e P/\pi\hbar^4)\int_0^\pi |M(\mathbf{P}, \mathbf{P'})|^2(1 - \cos\theta) \sin\theta d\theta, \qquad (A.36)$$

where θ is the angle between $\mathbf{P}$ and $\mathbf{P'}$. Using (A.34), and assuming c_l to be a constant, we find:

$$1/\tau = m_e PE_1^2k_0T/\pi\hbar^4c_{ii}. \qquad (A.37)$$

The mean free path, given by

$$1/l = 1/\tau v = m_e^2 E_1^2k_0T/\pi\hbar^4c_{ii}, \qquad (A.38)$$

is independent of the velocity of the electron. The mobility is

$$\mu = \frac{4el}{3(2\pi m_e k_0T)^{\frac{1}{2}}} = \frac{2(2\pi)^{\frac{1}{2}}e\hbar^4c_{ii}}{3m_e^{5/2}(k_0T)^{\frac{3}{2}}E_1^2}. \qquad (A.39)$$

For comparison with experiment it is convenient to express μ in practical units, cm^2/volt-sec., and to express the energy constant, E_1, in electron volts. If the effective mass, m_e is set equal to the ordinary electron mass, and the constant factor is evaluated, it is found that

$$\mu T^{\frac{3}{2}} = (3.2 \times 10^{-5})c_{ii}/E_1^2. \qquad (A.40)$$

Solving for E_1 gives

$$E_1^2 = (3.2 \times 10^{-5})\rho c_l^2/\mu T^{\frac{3}{2}}. \qquad (A.41)$$

Equation (47) can be used to determine $|E_{1c}|$ and $|E_{1v}|$ for the conduction and valence-bond bands respectively from observed values for the mobilities of conduction electrons and holes. The values of c_{ii} are obtained in terms of the cubic elastic constants in Section IV.