picture of the acceptor levels according to Shockley and Read is the following. Slip in these crystals takes place along the \{111\} planes and along a (110) direction. The extra half plane associated with an edge dislocation leads to a row of "dangling" bonds since the atoms of this row have no neighbors on one side. An electron paired with one of those dangling bonds would not be as "free" as an electron in the conduction band, so that the corresponding level should lie below the bottom of the conduction band. On the other hand, the paired electron is not as strongly bound as one corresponding to a normal electron pair bond between two neighboring atoms, i.e., the level associated with the dangling bond should lie above the filled band. Consequently, an edge dislocation corresponds to a row of acceptor levels lying in the forbidden energy region. For a detailed discussion of the implications of this model for the electrical properties of these materials we refer the reader to a series of three papers by Read.\(^{17}\)

13-3. Conductivity and Hall effect in semiconductors with a single type of charge carrier

Before discussing the electrical properties of Si and Ge, some remarks on the conductivity and Hall effect of semiconductors should be made. In this section we shall limit ourselves to the case of a single type of charge carrier. The conductivity of such a material is given by

\[ \sigma = ne\mu \]  \hspace{1cm} (13-2)

where \( n \) is the density of carriers and \( \mu \) is their mobility (drift velocity per unit field). It is observed that measurements of \( \sigma(T) \) provide information only about the product \( n(T)\mu(T) \), and in general do not allow one to determine these quantities separately. However, if we assume for the moment that the Hall coefficient for a semiconductor is given by the formula applicable to metals we would have (see 11-65),

\[ R_H = 1/n\epsilon_c \quad \text{and} \quad c\sigma R_H = \mu \]  \hspace{1cm} (13-3)

Thus \( R_H(T) \) would provide information about \( n(T) \), and combined measurements of \( R_H \) and \( \sigma \) thus permit determination of \( n \) and \( \mu \) separately. Although this type of analysis is indeed applied to semiconductors, there are some modifications in the formula for \( R_H \) which will be discussed below. Also, the temperature-dependence of \( \mu \) is different from that for metals.

We shall give here a simple theory for \( n \)-type material based on the assumption that the electrons in the conduction band behave as nearly free electrons with an effective mass \( m^* \); this implies that constant-energy surfaces in momentum space are assumed to be spheres. There exists at

\(^{17}\) W. T. Read, Phil. Mag., 45, 775 (1954); 45, 1119 (1954); 46, 111 (1955).
present a great deal of evidence (see Sec. 13-6) that this is not correct, but in many instances the simple theory still gives rather good agreement with the experiments. It is also assumed that the electron gas in the conduction band is nondegenerate, and thus that it has a Maxwellian distribution.

As an example, consider a semiconductor in which the current is carried only by electrons in the conduction band. Suppose an electric field \( E_x \) and a magnetic field \( H_z \) are applied to the material as indicated in Fig. 13-5. The current density \( I_x \) along the \( x \)-direction may then be obtained from the Boltzmann transport equation in the same way as for metals. Thus from (11-28) it follows that

\[
I_x = -\frac{e^2 E_x}{3} \int_0^\infty \frac{\partial F_0}{\partial E} v^2 \tau(E)(8\pi\hbar^2) p^2 dp
\]

(13-4)

The relaxation time \( \tau \) is assumed to be a function only of the energy of the electrons, not of their direction of motion. Now it can readily be shown that the Fermi function \( F_0(E) \) satisfies the relation

\[-(\partial F_0/\partial E) = F_0(1 - F_0)/kT \approx F_0/kT\]

(13-5)

The last approximation is valid only if the density of the electrons in the conduction band is small enough so that \( F_0 \ll 1 \), i.e., if the system is nondegenerate. Recognizing that \( 8\pi p^2 dp F_0/\hbar^2 \) equals the number of electrons with momentum in the range \( dp \), it follows that

\[
I_x = \frac{ne^2 E_x}{3kT} \langle v^2 \tau \rangle = \sigma E_x = ne\mu E_x
\]

(13-6)

Here \( \langle v^2 \tau \rangle \) is the average value of \( v^2 \tau(E) \), the average being taken over the Maxwellian distribution of the conduction electrons. Since \( 3kT = m^* \langle v^2 \rangle \), one may also express the mobility as

\[
\mu = \frac{e}{m^*} \frac{\langle v^2 \tau \rangle}{\langle v^2 \rangle}
\]

(13-7)

Note that if \( \tau \) were independent of the velocity of the electrons, this would reduce simply to \( \mu = e\tau/m^* \), as in the simplified model discussed in Sec. 11-2. We shall return to this expression in the next section.
The Hall effect may be discussed by considering the case for which the front and back faces in Fig. 13-5 are short-circuited, allowing the flow of a current along the \(y\)-direction. An electron of velocity \(v_x\) under influence of the magnetic field \(H_z\) will develop a velocity along the \(y\)-direction such that

\[
(\partial v_y/\partial t)_{H_z} = e v_x H_z/m^*c = \omega v_y
\]  

(13-8)

On the other hand, due to collisions with the lattice,

\[
(\partial v_y/\partial t)_{\text{coll}} = -v_y/\tau
\]

Hence, in the steady state,

\[
v_y = e v_x H_z \tau/m^*c = \omega \tau v_x
\]  

(13-9)

In analogy, one may thus obtain the current along the \(y\)-axis by multiplying the integrand of (13-4) by \(\omega \tau\). This finally leads to

\[
I_y = \langle ne^2 E_y \omega /3kT \rangle \langle \nu_2 \tau^2 \rangle
\]  

(13-10)

Thus, although the electric field is applied along the \(x\)-direction, the resultant current has a \(y\)-component due to the magnetic field. In fact, it is convenient to define the Hall angle \(\theta_H\) (see Fig. 13-5), where

\[
\tan \theta_H = \theta_H = I_y/I_x = \omega \frac{\langle \nu_2 \tau^2 \rangle}{\langle \nu_2 \tau \rangle}
\]  

(13-11)

If the Hall contacts are not short-circuited, a field \(E_y\) is set up to counteract the influence of the magnetic field. The Hall coefficient then becomes

\[
R_H = E_y/I_x H_z = I_y/\sigma I_x H_z = \frac{1}{ne^2 c} \frac{\langle \nu_2 \tau^2 \rangle \langle \nu_2 \rangle}{\langle \nu_2 \tau \rangle^2}
\]  

(13-12)

where \(\sigma\) has been substituted from (13-6). Note that the sign of the carrier in the above derivation is contained in \(e\); for electrons \(R_H\) is negative, for holes it is positive. It should be mentioned that one frequently employs the Hall mobility \(\mu_H\) defined in analogy with (13-3) by

\[
\mu_H = c\sigma R_H = \frac{e}{m^*c} \frac{\langle \nu_2 \tau^2 \rangle}{\langle \nu_2 \tau \rangle}
\]  

(13-13)

Comparing this with the "normal" mobility given by (13-7), it is observed that in general \(\mu_H\) is not equal to \(\mu\).

From the foregoing discussion it is evident that the relaxation time \(\tau\) plays an essential role in the interpretation of conductivity and Hall effect data. The relaxation time in general is determined by collisions of the carriers with

(i) Lattice vibrations
(ii) Ionized impurities
(iii) Neutral impurities, dislocations, vacancies, and interstitials.
13-4. Mobility and Hall effect as determined by different scattering processes

(i) Scattering by lattice vibrations. From the theory of interaction of thermal electrons with lattice vibrations in nonpolar solids,\(^1\) it follows that

(a) The scattering is isotropic.

(b) The mean free path \(\Lambda\) is independent of the velocity of the carriers.

(c) The mean free path is inversely proportional to \(T\), down to temperatures of the order of \(1^\circ\)K.

The selection rules for electron-phonon interaction mentioned in Sec. 11-7 play an essential role in arriving at these conclusions. For a given temperature it thus follows from (a) and (b) that one may write\(^1^0\)

\[ \tau = \Lambda/\nu \]  
\[ (13-14) \]

Substituting \(\tau\) into the results obtained in the preceding section, one is thus left with the simple problem of finding averages over a Maxwellian distribution of quantities on the type \(v^n\). Thus, if only lattice scattering is present, (13-7) and (13-13) give

\[ \mu = \frac{3e\Lambda}{(2\pi nkT)^{1/2}} \quad \text{and} \quad \mu_\parallel = (3\pi/8)\mu \]  
\[ (13-15) \]

Combining this result with (c) above, one concludes that the mobility \(\mu\) should be proportional to \(T^{-3/2}\) in this case. Bardeen and Shockley\(^1^8\) find from their calculation of \(\Lambda\),

\[ \frac{e\tau}{m^*} = \mu = \frac{(8\pi)^{1/2}k^3c_{11}}{3E_1^2m^{*5/2}(kT)^{3/2}} = \text{const.} \ T^{-3/2} \]  
\[ (13-16) \]

Here, \(c_{11}\) is the average longitudinal elastic constant, and \(E_1\) is the shift of the edge of the conduction band per unit dilation; the temperature-dependence of both these quantities may be neglected. For holes, \(E_1\) represents the shift of the edge of the valence band per unit dilation. Experiments indicate that \(E_1 \simeq 10\) ev for germanium. The formula obtained by Seitz\(^1^8\) is written in terms of the Debye temperature \(\theta\), the mass \(M\) of the atoms, and their number per unit volume \(N\),

\[ \mu = \frac{2^{1/2} \times 6^{1/3}}{4\pi^{5/6}} \cdot \frac{N^{1/3}e^2h^2k^2\theta^2M}{m^{*5/2}C^2(kT)^{3/2}} \]  
\[ (13-16a) \]

The constant \(C\) has the dimensions of an energy and is of the same order of magnitude as \(E_1\) in the Bardeen-Shockley formula; it is a measure for the electron-phonon interaction. The mobility determined by lattice scattering alone is usually referred to as the “lattice mobility.”


\(^1^9\) Compare expression (11-11) for the relation between collision time, relaxation time, and scattering angle.
The Hall coefficient as determined by lattice scattering for semiconductors containing one or two types of carriers is given, respectively, by

\[ R_H = \pm \frac{3\pi}{8ne_c} \quad \text{and} \quad R_H = \frac{3\pi}{8ec} \cdot \frac{n_h\mu_h^2 - n_e\mu_e^2}{(n_h\mu_h + n_e\mu_e)^2} \]  

where the subscripts \( e \) and \( h \) in the last formula refer to electrons and holes, respectively. The conductivity for two types of carriers is of course equal to \( n_e\mu_e + n_h\mu_h \).

(ii) Ionic scattering predominates. When the concentration of ionized donors is high, the charge carriers suffer Rutherford scattering due to the presence of ions, as illustrated in Fig. 13-6. If one assumes that the ions are distributed throughout the lattice in a regular fashion, the average distance between the ions \( a_i \) is given by \( a_i^2 = 1/N_i \), where \( N_i \) is the number of ions per unit volume. Thus if \( v \) is the velocity of an electron, the mean free time between collisions is \( \tau_c = a_i/v \). The relaxation time according to (11-11) is in general given by

\[ \tau = \tau_c(1 - \langle \cos \beta \rangle) \]

where \( \langle \cos \beta \rangle \) is the average of the cosine of the scattering angle. Making use of the Rutherford scattering formula, Conwell and Weisskopf have calculated an approximate expression for \( \tau \) with the result that

\[ \mu = \frac{er}{m^*} = \frac{e^2m^*e^3}{2\pi Ne^3} \left[ \log \left( 1 + \frac{e^2m^*a_i^2}{4e^2N_i^2e^3} \right) \right]^{-1} \]  

where \( e \) is the dielectric constant.\(^{20}\) It is observed that this type of scattering leads to a mobility which varies approximately as \( T^{3/2} \), in contrast with the \( T^{1/2} \) law for lattice scattering.

The Hall coefficient and Hall mobility associated with ionic scattering are found to be \(^{21}\)

\[ R_H = \pm 1.93/ne_c, \quad \mu_H = 1.93\mu \]

(iii) Neutral impurity scattering. The scattering of charge carriers by neutral impurities is quite similar to the scattering of electrons by hydrogen


\(^{21}\) W. Shockley, *op. cit.*, p. 279.
atoms. Thus, by suitably modifying the theory of the latter, Erginsoy has calculated the mobility associated with this type of scattering alone.\textsuperscript{22} He finds
\[
e\tau/m^* = \mu = \frac{m^*e^3}{20N\epsilon\hbar^2}
\] (13-20)

where \(N\) is the density of neutral impurities and \(\epsilon\) is the dielectric constant. The relaxation time is independent of the velocity in this case, so that the Hall coefficient is the same as that for metals, viz., \(R_H = \pm 1/\rho e\), as can readily be seen from (13-12).

Dislocations are also scattering centers for charge carriers as a result of the dilation they produce in the lattice. According to calculations by Dexter and Seitz the probability for scattering is proportional to the number of dislocation lines per cm\(^2\) and proportional to the temperature \(T\).\textsuperscript{23}

Scattering of charge carriers by vacancies and interstitials is used in studying radiation effects in solids by resistivity measurements.

In general, lattice scattering, ionic scattering, and scattering by neutral impurities are all present. The relaxation time for a given velocity of the charge carriers may then be obtained from
\[
1/\tau = 1/\tau_{\text{lattice}} + 1/\tau_{\text{ionic}} + 1/\tau_{\text{neutral}}
\] (13-21)
because the probabilities for scattering are additive, each of them being proportional to the reciprocal of the corresponding relaxation time.

13-5. Comparison with experiment

The first extensive investigation of the electrical properties of the elements of the fourth group was carried out by Pearson and Bardeen on silicon and silicon alloys containing boron and phosphorus.\textsuperscript{24} In these experiments polycrystalline materials were used. More recently, the electrical conductivity and Hall effect of single crystals of silicon containing arsenic (\(n\) type) and boron (\(p\) type) have been studied by Morin and Maita over a temperature range between 10\(^0\)K and 1100\(^0\)K.\textsuperscript{25} The mobilities in single crystals are appreciably larger than those in polycrystalline materials (see Table 13-3). Similar measurements on germanium crystals containing arsenic have been reported by Debye and Conwell; these extend over the temperature range between 11\(^0\)K and 300\(^0\)K.\textsuperscript{26}

As an example we reproduce in Fig. 13-7 and 13-8 the resistivity and Hall coefficient for some of the samples measured by Debye and Conwell, (they actually measured eleven samples). The intrinsic resistivity is indicated by the dashed line in Fig. 13-7. Sample 55 is nearly pure, whereas sample 58 contains enough arsenic to make the electron gas in the conduction band degenerate over most of the temperature range. The other samples have intermediate impurity densities.

In accordance with (13-13), the Hall mobility may be obtained from the relation \( \mu_H = eR_H/\rho \); the results are given in Fig. 13-9. It is observed that the nearly pure sample 55 follows closely the \( T^{-3/2} \) law down to the lowest temperatures. The reason for this is that neutral impurity scattering
and ionic scattering are negligible for low impurity concentrations. As the impurity concentration increases, ionized donors become important as scattering centers at lower temperatures where the amplitude of the lattice vibrations becomes small. Sample 61 contains a sufficient number of ionized donors at low temperatures to give a positive slope for the $\mu(T)$ curves. In most of the samples, however, the slope gets steeper again after the initial flattening resulting from ionic scattering; the reason for this is that electrons fall back into donor levels at low temperatures, thus reducing the influence of ionic scattering.

A quantitative analysis of these results shows that in the range where scattering of electrons by the lattice is predominant, the mobility varies as $T^{-1.64}$ rather than as $T^{-1.5}$. This deviation from the simple theory is probably in part due to the fact that the constant energy surfaces in the momentum space are not spheres. We shall return to this in Sec. 13-6. Similar deviations have been observed by Morin and Maita for silicon. A summary of mobility data is given in Table 13-3.

![Fig. 13-9. Hall mobility for some arsenic-doped germanium samples as function of $T$; the sample numbers are the same as those in Figs. 13-7 and 13-8. [After Debye and Conwell, ref. 26]]

<table>
<thead>
<tr>
<th>Table 13-3. Mobilities in cm$^2$ volt$^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>C (diamond), electrons$^a$ 900</td>
</tr>
<tr>
<td>Si (polycryst.) electrons  300</td>
</tr>
<tr>
<td>Si (polycryst.) holes  100</td>
</tr>
<tr>
<td>Si (single cryst.) electrons  1450</td>
</tr>
<tr>
<td>Si (single cryst.) holes  500</td>
</tr>
<tr>
<td>Ge (single cryst.) electrons  3600</td>
</tr>
<tr>
<td>Ge (single cryst.) holes  1700</td>
</tr>
<tr>
<td>Sn (grey) electrons$^b$  3000</td>
</tr>
</tbody>
</table>


Debye and Conwell conclude from their measurements that the mobility associated with ionic scattering increases with a power of $T$
between 1.0 and 1.5, i.e., less rapidly than predicted by the Conwell-Weisskopf formula. The Erginsoy formula for neutral impurity scattering fits their data well for an effective electron mass equal to about \( m/3 \). They find scattering by dislocations negligible in their samples.

13-6. Constant-energy surfaces and effective mass in silicon and germanium

The theory developed in Sec. 13-3 and 13-4 was based on the assumption that the energy of electrons near the bottom of the conduction band or of holes near the top in the valence band could be represented by \( \hbar^2 k^2/2m^* \). This implies that constant-energy surfaces in \( \mathbf{k} \)-space are spheres and that \( m^* \) is a constant independent of the direction of motion of the carriers. It is presently believed that the discrepancies between theory and experiment cited above are, at least in part, due to the fact that this assumption is incorrect. Thus values of the effective mass calculated indirectly from the electrical properties must be considered unreliable. Measurements of the influence of a magnetic field on the resistivity of single crystals of germanium also drew attention to the fact that the constant-energy surfaces cannot be spheres.\(^{27}\)

If the constant-energy surfaces are spheres, the effective mass is, according to (10-38),

\[
m^* = \frac{\hbar^2}{(d^2E/dk^2)}
\]

However, if the energy is a function also of the direction of the wave vector \( k \), the effective mass is a tensor rather than a scalar, as was mentioned in Sec. 10-4. By a suitable choice of axes, this tensor may be diagonalized in such a way that along the three principal axes the effective mass is given by

\[
m^*_i = \frac{\hbar^2}{(d^2E(k)/dk_i^2)} \quad \text{where} \quad i = x, y, z \quad (13-22)
\]

For example, for motion along the x-axis, the electron behaves as a particle of effective mass \( \hbar^2/(d^2E/dk_x^2) \), etc. Until recently, experimental information about the effective mass, and hence about the curvature of constant-energy surfaces in the \( \mathbf{k} \)-space, could be obtained only indirectly, viz., from experimental results for transport phenomena in which \( m^* \) occurs. However, cyclotron resonance experiments of electrons and holes have made it possible for the first time to measure \( m^* \) directly.\(^{28}\) In this type of experiment, electrons in the conduction band and holes in the valence band describe spiral orbits about the axis of a constant magnetic field \( H \).

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