**Completely Compensated Crystalline Semiconductor as a Model of an Amorphous Semiconductor**

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It is shown that large-scale potential fluctuations of magnitude comparable with the forbidden band width exist in a completely compensated semiconductor with randomly distributed donors and acceptors. The allowed bands are bent by these fluctuations so that they intersect repeatedly the Fermi level, forming electron and hole drops. A relationship is derived between the concentration of charged impurities, the characteristic scale of fluctuations, and the densities of electrons and holes. The absorption coefficient of such a semiconductor decreases rapidly when the photon energy becomes less than the forbidden band width. Electrical conduction is an activated process with an activation energy slightly smaller than half the forbidden band width. It is shown that a system of this type can be regarded as a model of an amorphous semiconductor.

**INTRODUCTION**

Optical absorption experiments indicate that the allowed and forbidden bands of amorphous semiconductors are divided by sharp boundaries. On the other hand, microwave absorption and other experiments suggest a high density of states at the Fermi level located approximately in the middle of the forbidden band. Fritzschke\(^1\) has suggested that these observations can be reconciled if we assume that the short-range potential associated with the absence of a periodic structure produces practically no states in the forbidden band. This is why the absorption coefficient of light falls sharply when the photon energy becomes less than the forbidden band width \(E_g\). Moreover, Fritzschke has suggested the existence of large-scale fluctuations of the electrostatic potential of amplitude of the order of \(E_g\). The bottom of the conduction band and the top of the valence band repeat the fluctuations of this potential so that the optical width of the forbidden band remains constant. Nevertheless the energy of states at the Fermi level may be high, as shown in Fig. 1 which gives the energy scheme of a completely compensated semiconductor. However, Fritzschke did not indicate how these large-scale fluctuations arise and what determines their amplitude. We shall show that these fluctuations may be due to a random distribution of positive and negative charged centers and we shall express the scale of the fluctuations in terms of the concentration of such centers \(N\) and the forbidden band width \(E_g\).

We shall consider a model which basically represents a heavily doped and completely compensated crystalline semiconductor containing \(N/2\) donors and \(N/2\) acceptors per unit volume. This will allow us to use the effective mass in the description of the electron and hole states. We shall derive a relationship between the optical and electrical widths of the forbidden band, the law governing the fall in the absorption coefficient of light within the forbidden band, and the densities of electrons and holes. Some of the results obtained are independent of the effective mass approximation and they can definitely be applied to an amorphous semiconductor. Other conclusions should be applied to amorphous materials with care.

The theory of strongly compensated semiconductors put forward in the present paper is also of intrinsic interest. Semiconductors with a very high degree of compensation are being currently manufactured. For example, Redfield and Crandall\(^2\) reported the preparation of a sample of gallium arsenide in which the concentrations of donors and acceptors differ only by 0.001%. At these very high degrees of compensation, the energy scheme of a semiconductor resembles that shown in Fig. 1. In Sec. 1 we shall give a qualitative derivation of the physical situation shown in Fig. 1. We shall support this by a rigorous theory in Sec. 2 and we shall study the asymptotic properties of the density of states. Finally, in Sec. 3 we shall discuss the observable effects and the possibility of application of our theory to amorphous semiconductors.

1. **ELECTRON STATES IN A COMPLETELY COMPENSATED SEMICONDUCTOR (QUALITATIVE CONSIDERATIONS)**

Let us consider a completely compensated semiconductor which contains \(N/2\) donors and \(N/2\) acceptors per unit volume. For simplicity we shall assume that the heavy doping condition is satisfied for electrons and for holes, i.e., that the concentration \(N\) satisfies the inequalities

\[
N_e > 1, \quad N_h > 1,
\]

where \(a_e = \hbar^2 k_e / m_e e^2\) and \(a_h = \hbar^2 k_h / m_h e^2\) are the Bohr radii of an electron and a hole. Here, \(m_e\) and \(m_h\) are the masses of an electron and a hole, and \(\kappa\) is the permittivity. In this case, electrons and holes in collective states (the impurity bands merge with the conduction bands), and donors and acceptors are charged positively and negatively, respectively. If donors and acceptors were distributed uniformly in space, electrons and holes would have completely recombined at 0\(^\circ\)K. This situation would represent an intrinsic semiconductor with its Fermi level in the middle of the forbidden band.
bend an allowed band by an amount of the order of $E_g$. At impurity concentrations small the smallest size $R_g$ of a typical fluctuation which can and holes would appear in this band. The number of electron states $R_g$ and depth $E_g$ is also arbitrary large. However, we can readily show that no fluctuations of the potential exceeding $E_g/2$ can exist. If, in some region, an excess of positively charged impurities depresses the bottom of the conduction band below the Fermi level, the number of electrons which will appear in this volume will be sufficient to prevent further depression of the conduction band (Fig. 1).

Similarly an excess of negatively charged impurities cannot raise the bottom of the conduction band by an amount greater than $E_g/2$ because then the top of the valence band would be shifted above the Fermi level and holes would appear in this band. We shall determine the smallest size $R_g$ of a typical fluctuation which can bend an allowed band by an amount of the order of $E_g$. If we use Eq. (1), we obtain the following relationships for $R_g$:

$$\gamma(R_g) = E_e, \quad R_e = \frac{E_e}{\gamma(R_g)}.$$

The number of electron states $\gamma(R_g)$ in a well of width $R_g$ and depth $E_g$ is

$$\gamma(R_g) = \frac{h^2}{\pi m_e} \left( \frac{2m_e}{h^2} \right)^{3/2} R_g.$$

(Here, and throughout the qualitative discussion in Sec. I we shall ignore the numerical factors.) The excess charge of impurities in such a well is $Z(R_g) = (NR_g^2)^{3/2}$. At impurity concentrations small compared with the concentration of host atoms, a typical semiconductor satisfies the inequality

$$a_i = \frac{Z(R_g)}{\gamma(R_g)} = \left( \frac{e^2N_i}{|eE_g|} \right)^{3/2} (Na_i)^3 < 1.$$  \hspace{1em} (4)

This means that the electrons necessary for the compensation of the charge in a well of width of $R_g$ can be located in the lowest states. In other words, the bottom of this well can drop below the Fermi level only to a depth which is small compared with the depth of the well, as shown in Fig. 1. It follows clearly that a fluctuation of size exceeding $R_g$ is neutralized by electrons and holes, i.e., that $R_g$ behaves as the screening radius of the impurity potential.

Thus, large-scale fluctuations transform an intrinsic semiconductor in a system resembling a semimetal. At $T = 0°K$ this system comprises a fairly large number of electrons and holes which are isolated in space. For this reason the static conduction in the system is not of metallic nature.

A well of size $R_g$ may have dips and humps due to small-scale fluctuations. Naturally, electrons and holes will fill such dips (Fig. 1). Let us assume that the scale of fluctuations of the impurity potential is at least $L$, where $L \ll R_g$. Then, electrons and holes form drops of size $L$, which occupy small-scale dips located within deep large-scale wells. The number of electrons and holes in such drops is limited by the impurity charge and, consequently, it is equal to $(NL)^{3/2}$, whereas the density of carriers in the drops is $n(L) = L^3/(NL)^{3/2}$. When $L$ decreases, these drops break up more and more and the density of electrons and holes in the drops increases.

We recall that the number of electrons in a well is limited not only by the impurity charge but also by the Pauli principle. In a well of depth $\gamma(L)$ the number of states is $\gamma(L) = h^2/(m_e \gamma(L) L)^{3/2} L$. For low values of $L$ the number of states is $\gamma(L) < (L^3)^{1/2}$ and the quantum restrictions become more important than the charge limitations. We shall introduce a length $R_e$ corresponding to the transition from the charge to the quantum restrictions:

$$\gamma(R_e) = (NR_e)^3, \quad R_e = a_i / (Na_i)^3.$$ \hspace{1em} (5)

We shall now show that when $L < R_e$ the drops no longer break up, i.e., the basic size of electron drops is $R_e$. We can easily show that the length $R_e$ is that value of $L$ at which the Fermi energy of electrons of density $n(L)$ becomes comparable with the depth of the well $\gamma(L)$. Fluctuations of the impurity potential whose scale is $L < R_e$ do not split up the drops because the humps and dips produced by these fluctuations are characterized by values of $\gamma(L)$ which are smaller than the Fermi energy of electrons in a drop $\gamma(R_e)$. In other words, such humps do not give rise to islands in the electron sea.

Similarly, we can show that the characteristic size of a hole drop is $R_h = a_i / (Na_i)^3$. It follows from Eq. (4) and from the corresponding inequality containing $a_i$ that $R_e, R_h < R_g$ and $\gamma(R_e), \gamma(R_h) < E_g$. The drop charges $e(NR_e^2)^{1/2}, e(NR_h^2)^{1/2}$ are small compared with...
the charge $e(N_A \rho_{\text{avg}})^{1/2}$ of a region of size $R_g$. Therefore, a large number of drops participates in the screening of each of the large-scale fluctuations. Since the masses of electrons and holes are different, the charges and dimensions of the electron and hole drops are different and the numbers of drops screening identical positive and negative charges are also different. However, the charge symmetry of the screening is restored completely by averaging over a region larger than the average distance between drops. Since the probabilities of positive and negative fluctuations of impurities in a random distribution are equal, the statistical properties of the resultant large-scale potential (which includes the potential of electrons and holes) are symmetrical with respect to a change in the sign of the potential. Hence, it follows that at $T = 0$ the Fermi potential can be taken as located in the middle of the forbidden band, provided we ignore terms of the order of $e^2/n^2 \rho^2$, where $n^2 \rho^2$ is the average distance between drops.

The Fermi level, $\mu$, is found by equating the average densities of electrons $n_e$ and holes $n_h$.

It is convenient to carry out the averaging of Eqs. (8) and (9) not over space but over all the values of $V$ by means of a distribution function $F(V)$. For example, the averaging of the electron density yields

$$n_e = \frac{(2m_e)^{1/2}}{3\pi h^2} \int (y - V)^{1/2} F(V) dV.$$  

By definition, $F(V)$ is given by

$$F(V) = \int e^{-(y-V)/E_F} dV / \int e^{-(y-V)/E_F} dV.$$  

Here, the functional integration is carried out over all the functions $\xi = N_D(r) - N_A(r)$, and $V(\xi)$ is a functional representing a local solution of Eq. (7), which vanishes at infinity. The quantity $\exp(-\Omega(\xi))$ is the probability of a fluctuation $\xi$. We shall be interested in Gaussian fluctuations \( (13) \) which satisfy

$$\Omega(\xi) = \frac{1}{2N_e} \int V' \xi^2.$$

Following the discussion in Sec. 1, we shall introduce the dimensionless variables

$$x = \frac{r}{R_g}, \quad \gamma(x) = \frac{V(r)}{E_F}, \quad \xi(x) = \frac{\xi(x)}{n_e} = \frac{\eta - \mu}{E_F},$$

where $R_g$ and $n_e$ are given by Eqs. (2) and (6). In terms of the new variables we obtain

$$\Delta x = 4\pi (f + p_h - p_e),$$

where

$$p_e = \left\{ \begin{array}{ll} 0, & \xi < \eta \\ \frac{2^\nu (\xi - \eta)^{1/2}}{\pi^{1/2}}, & \xi > \eta \end{array} \right.$$  

$$p_h = \left\{ \begin{array}{ll} 0, & \xi < \eta + 1 \\ \frac{2^\nu (\xi - \eta - 1)^{1/2}}{\pi^{1/2}}, & \xi > \eta + 1 \end{array} \right.$$  

Here, $\sigma_e$ is given by Eq. (4) and $\sigma_h$ is found from $\sigma_e$ by replacing $m_e$ with $m_h$. The random Gaussian distribution $\xi(x)$ is described by the correlation function

$$\langle f(x) f(x') \rangle = \delta(x - x').$$

We shall still assume that $\sigma_e, \sigma_h \ll 1$. It then follows from Eqs. (14)–(16) that in the regions where $\rho_e > 0$ the potential energy is almost constant and close to $\eta$. In this case, $\rho_e = t$. In the regions where $\rho_h > 0$, we find that $\eta = \eta + 1$ and $p_h = t$. Thus, we are facing the following problem. A continuous charge density $f(x)$ is given. We must find regions $Q_e$ and $Q_h$ which have the following properties:

1) $f(x) > 0$ in $Q_e$ and $f(x) < 0$ in $Q_h$;

2) if all the charges contained within $Q_e$ and $Q_h$ are removed, the remaining charges establish a constant potential $\chi = \eta$ inside $Q_e$, a potential $\chi = \eta + 1$ inside $Q_h$, and a potential $\chi$, satisfying the inequalities $\eta < \chi < \eta + 1$ outside $Q_e$ and $Q_h$;

3) the chemical potential $\eta$ is found by equating to zero the total charge outside $Q_e$ and $Q_h$.

The problem facing us has no adjustable parameters and this shows that the characteristic value of the
potentials is of the order of $E_g$ and the characteristic size of fluctuations is of the order of $R_g$. The characteristic size of the regions $O_E$ and $O_H$ is of the order of the smallest scale $L$ considered in modeling the random function $f(x)$. We shall be interested in the value of $\eta$ which is obtained in the limit as $L \to 0$.

Actually, the classical approximation which we have used becomes invalid in the case of very small scales of the function $f$. This gives rise to the formation of electron and hole drops (for details see [31]). Since the dimensions of these drops are $R_e, R_h \ll R_g$, the quantum corrections to the classical value of $\eta$ are small.

The electrostatic problem formulated above has the following important symmetry. In this problem the chemical potential $\eta$ is a self-averaging quantity, i.e., it is independent of the actual realization of the random function which is specified in a fairly large spatial region and which satisfies the correlation relationship (17). Let us assume that we have found the regions $O_E$ and $O_H$ for some realization of $f(x)$. We shall assume that another realization is the function $F'(x) = -f(x)$, which also satisfies Eq. (17). We can easily show that the solution of the problem for the new realization is represented by regions $O_E$, which are identical with the old regions $O_H$, and regions $O_H$, which are identical with the old regions $O_E$. The potential in the $O_E$ regions and, consequently, the new chemical potential are both given by $\eta' = -\eta - 1$. It follows from $\eta' = \eta$ that $\eta = -\frac{1}{2}$, i.e., in the classical approximation the chemical potential is located exactly in the middle of forbidden band. The function $F(V)$ should also be independent of the realization of the random function. When the substitution $V \to -V$ is made, the sign of the potential $V$ is reversed. Consequently, $F(V)$ is an even function: $F(V) = F(-V)$. Similarly we can show that all the odd correlation functions $V(x)$ vanish.

These symmetry properties apply only to the large-scale fluctuations of the potential which can be studied ignoring the quantum effects.

An analysis of the asymptotic properties of the solutions of Eqs. (7)–(9) can give us a better idea on the nature of these solutions within the carrier drops. We shall find first the law which describes the fall of the function $F(V)$ for $V < \mu$ and $V > \mu + E_g$. Since this law is exponential, we can find it by the optimal fluctuation method.[11] We shall consider first the electron drops in which $\mu - V(r) > 0$. The idea behind this method is to find the function $\tilde{f}(x)$ which gives rise to a minimum of the functional $\Omega(\tilde{f})$, subject to the additional condition $\tilde{f}(x) = \epsilon \to \epsilon > 0$. In the region where $\tilde{f}(x) \to 1$, we find that

$$\ln F(\mu - \epsilon) = -\Omega(\tilde{f}).$$  \hfill (18)

We shall find it convenient to rewrite Eq. (7) in terms of the following new variables:

$$q(y) = \frac{\mu - V(r)}{\epsilon}, \quad y = r e^{\frac{\mu v(r)}{E_g}}, \quad \theta = \frac{\gamma \theta_0}{(m, e)^{1/2}}.$$ \hfill (19)

Then, instead of Eq. (7), we obtain

$$\Delta q = -4\pi \left[ \theta(\gamma - 1) - \frac{2\gamma}{\sinh \gamma} q_0 \right].$$ \hfill (20)

and the functional $\Omega(\theta)$ becomes

$$\Omega(\theta) = \left[ \frac{\epsilon}{\sqrt{\gamma} \gamma \theta_0} \right] \gamma \theta_0 \int \theta(y) dy.$$ \hfill (21)

The extremal function $\tilde{q}(y)$ can be found from the condition

$$\delta \left( \int \theta(y) dy - t_\theta(\theta_0) \right) = 0,$$ \hfill (22)

where $\theta = \theta(y)$ is the solution of Eq. (20) taken at the center of a fluctuation (this solution vanishes at infinity). The Lagrange multiplier $t$ is found from the condition

$$\frac{\partial}{\partial \theta} \int \theta(y) dy = t.$$ \hfill (23)

The system of equations (20), (22), and (23) contains no parameters and, consequently, $\tilde{q}(y)$ is a unique function. Using Eqs. (18) and (21), we find that

$$\ln F(\mu - \epsilon) = -\lambda(\gamma) \gamma \theta_0 (\gamma \theta_0) \gamma \theta_0 \int \theta(y) dy.$$ \hfill (24)

where

$$\lambda = \frac{1}{4} \int \tilde{q}(y) dy$$

is a numerical coefficient which can be determined as described above. It is evident from Eq. (24) that in a typical electron drop (the probability of whose existence is not exponentially small) the bottom of the conduction band is located below the Fermi level and the gap between the two is of the order of $\gamma(R_e)$. Since in the case of an optimal fluctuation $y = 1$, it follows from Eq. (19) that the size of the electron drop is $R_e$. Similarly we can find that when $V - \mu - E_g \gg \gamma(R_e)$,

$$\ln F(\mu - \epsilon) = -\lambda \frac{V - \mu - E_g}{\gamma(R_e)}.$$ \hfill (25)

3. MEASURABLE PROPERTIES

In this section we shall consider the most important experiments in which the structure of electron states discussed above can be manifested.

A. Static Conductivity

We can easily show that the volume occupied by electron and hole drops represent a small fraction of the total volume of a crystal. In fact, the total charge of electrons in one positively charged fluctuation of volume $R_e^3$ is of the order of the charge in this fluctuation $\epsilon(R_e^3)^{1/2}$. The charge in one drop is $\epsilon(R_e^3)^{1/2}$. Therefore, the number of drops in such a fluctuation is $(R_g/R_e)^{3/2}$ and the fraction of the volume of the fluctuation occupied by the drops is $(R_e/R_g)^{3/2}$ and the fraction of the volume of the fluctuation occupied by the drops is $R_g/R_e^3$. For this reason the electron and hole drops do not form infinite bound chains and the static conductivity at the Fermi level is solely due to the tunnel effect. The tunneling probability contains a small factor $\exp\left(-\frac{2\pi e E_g}{m, e}^{1/2} R_e^3 R_g^3/3\right)$, Therefore, at moderate temperatures the electrical conductivity is due to electrons and holes transferred to their percolation levels $E_c$ and $E_h$. The percolation levels $E_c$ and $E_h$ can be found from Eqs. (14)–(17). Since these equations contain no parameters, the gap between the electron percolation level and the bottom of the unperturbed conduction band $E_c$ is comparable with $E_g$. Moreover, the symmetry of the statistical properties of the potential $V(x)$ shows that $E_c < E_g$. In fact, when the energy is $E_c$, half the space is occupied by classically permitted regions. In the case of percola-
tion in the three-dimensional case the critical fraction of occupied space is less than half.\[^{[8]}\] It also follows from the symmetry of the potential that \(E_e - \mu = \mu - E_h\).

Thus, the activation energies of electrons and holes are equal and are both less than \(E_g/2\). One of the present authors has given reasons\[^{[7]}\] why even in the case of an asymmetrical potential \(\min\{E_e - \mu, \mu - E_h\}\) is less than \(E_g/2\).

B. Interband Absorption of Light

The large-scale potential relief shown in Fig. 1 is classical in the sense that the probability of tunneling under the barriers is exponentially small. Therefore, such a relief does not reduce the optical width of the forbidden band. The absorption of light quanta with an energy deficit \(\Delta E < E_g\) does not reduce the optical width of the forbidden band. The latter hypothesis is supported strongly by the experimental data on the interband absorption of light. It follows from these classical equations that the activation energy of the static conductivity \(\Delta E\) is less than half the optical width of the forbidden band \(E_g/2\). One of the present authors has shown\[^{[7]}\] that this is in agreement with the experimental results. We note that in our model, which presupposes a random distribution of charged centers, the ratio \(\Delta E/E_g\) is independent of the parameters of the material. It can be found by numerical solution of Eqs. (14)–(17) and of the percolation problem. The deviations of \(\Delta E/E_g\) from the theoretical value may be due to correlation in the distribution of charged centers. The average density of carriers \(n_p\) generated as a result of band bending can also be calculated without recourse to the effective mass approximation. If we assume that the concentration of charged centers is \(N = 5 \times 10^{20} \text{cm}^{-3}\), we find from Eq. (6) that \(n_p = 10^{18} \text{cm}^{-3}\), which is close to the values obtained experimentally.\[^{[1]}\] The scales of lengths and energies associated with carrier drops must depend strongly on the validity of the effective mass approximation. This is also true of the law governing the law of fall of the interband absorption coefficient.

C. Absorption of Microwave Radiation

In contrast to the static conduction, all the electrons and holes in drops participate in the high-frequency conduction. The average number of carriers per unit volume, \(n_p\), is given by Eq. (6) and it can be quite high in spite of the fact that the Fermi level lies in the middle of the forbidden band.

D. S-Type Current-Voltage Characteristic

A strong electric field heats electrons and holes and the density of carriers transferred to the percolation levels increases. This may increase the current and enhance the heating of carriers still further. Therefore, when a sample is connected to a constant-current source, the resistance may decrease so much that the electric field decreases, i.e., the current-voltage characteristic may be of the S-type.\[^{[11]}\]

So far we have considered only a completely compensated crystalline semiconductor. We must now see whether the results can be applied to an amorphous semiconductor. The greatest difficulty is presented by the validity of the effective mass approximation in the case of an electron subject to a potential which is not strictly periodic. However, many of the results obtained are independent of the effective mass approximation. The classical equations (14)–(17) are simply based on the assumptions that the distribution of charged centers is random and that the local density of states decreases rapidly with depth in the forbidden band. The latter hypothesis is supported strongly by the experimental data on the interband absorption of light. It follows from these classical equations that the activation energy of the static conductivity \(\Delta E\) is less than half the optical width of the forbidden band \(E_g/2\). One of the present authors has shown\[^{[7]}\] that this is in agreement with the experimental results. We note that in our model, which presupposes a random distribution of charged centers, the ratio \(\Delta E/E_g\) is independent of the parameters of the material. It can be found by numerical solution of Eqs. (14)–(17) and of the percolation problem. The deviations of \(\Delta E/E_g\) from the theoretical value may be due to correlation in the distribution of charged centers. The average density of carriers \(n_p\) generated as a result of band bending can also be calculated without recourse to the effective mass approximation. If we assume that the concentration of charged centers is \(N = 5 \times 10^{20} \text{cm}^{-3}\), we find from Eq. (6) that \(n_p = 10^{18} \text{cm}^{-3}\), which is close to the values obtained experimentally.\[^{[1]}\] The scales of lengths and energies associated with carrier drops must depend strongly on the validity of the effective mass approximation. This is also true of the law governing the law of fall of the interband absorption coefficient.