



CHAPTER I

INTRODUCTION

1.1 Energy Band In Pure Semiconductors¹⁻⁷

In the study of the energy band in pure semiconductors, one starts by considering the behavior of a single electron among an array of fixed atoms. All other electrons and atomic nuclei may be assumed to produce static electrical field. Thus one is considering the behavior of an electron in a periodic structure as shown in Fig 1.1.

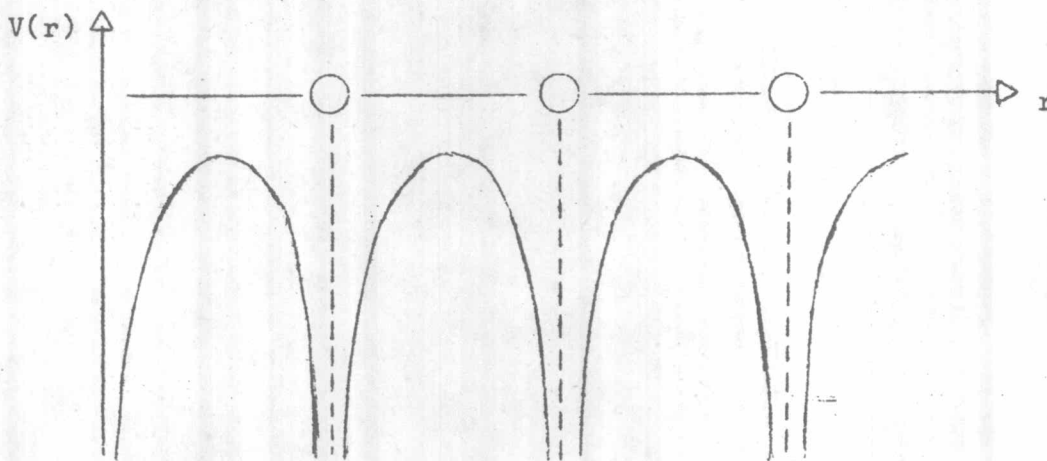


Fig 1.1 Potential energy function $V(\bar{x})$ of an electron in a one dimensional crystal

The electron may be considered as a wave propagating in a periodic structure with diffraction and interference effects. The Schrödinger equation describing the electron is written in the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) \quad 1.1.1$$

This equation can be solved with the aid of Bloch's theorem which states that one-electron wave function may be written in the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U_{n\vec{k}}(\vec{r}) \quad 1.1.2$$

where the wave vector \vec{k} is in the first Brillouin zone. $U_{n\vec{k}}(\vec{r})$ has the periodicity of the crystal and $n=1,2,3\dots$ is the band index. Thus all eigenfunctions of (1.1.2) are extended. There have been a number of attempts to calculate the band structure of solid by solving (1.1.1). As an example we note on the work of Kronig and Penny which gives a relationship between energy E and wave vector \vec{k} . They replace the actual periodic crystal potential by the rectangular shape at each lattice site. With the aid of Bloch's theorem they found that the corresponding energy to a particular value of \vec{k} was

$$E_{\vec{k}} = k^2 \hbar^2 / 8ma^2$$

Note that energy levels of an electron form bands separated by forbidden gaps. The formation of the bands makes the solid behaved as conductor, semiconductor and insulator.

Next we consider the energy bands in three dimensional lattice potential. We now face the problem which arises from the large numbers of bands involved. Consider the diamond structure where there are two atoms per primitive cell and four valence

electrons for each atom. Thus there are eight electrons per primitive cell occupying the bands. Fortunately it is not necessary to consider all of those bands. We need to consider the highest state in the valence band and the lowest state in conduction band, i.e., we consider only the state which lies within an energy of order $k_B T$ of the band edge where k_B is the Boltzmann's constant and T is the absolute temperature. There are a large numbers of theoretical calculation of band structures of pure semiconductors, i.e., Nearly Free Electron (N F E), Tight Binding, Linear Combination of Atomic orbital (L C A O) etc.

As an example we consider the N.F.E. method. From (1.1.1) using Bloch's theorem $V(\vec{r})$ can be expanded as Fourier series

$$V(\vec{r}) = \sum_{\vec{g}} V_{\vec{g}} \exp(i\vec{g} \cdot \vec{r}) \quad 1.1.3$$

where

$$V_{\vec{g}} = \frac{1}{\Omega_{\text{cell}}} \int_{\text{cell}} V(\vec{r}) e^{-i\vec{g} \cdot \vec{r}} d\vec{r}$$

and the solution is

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{g}} \alpha_{\vec{k}-\vec{g}} \exp[i(\vec{k}-\vec{g}) \cdot \vec{r}] \quad 1.1.4$$

Substituting $V(\vec{r})$ and $\psi_{\vec{k}}(\vec{r})$ into (1.1.1) and multiplying by

one of the term in the expansion, we get a linear equation for the coefficient α :

$$\left\{ \epsilon_{\vec{k}-\vec{g}}^0 - \epsilon(\vec{k}) \right\} \alpha_{\vec{k}-\vec{g}} + \sum_{\vec{g}} V_{\vec{k}-\vec{g}} \alpha_{\vec{k}-\vec{g}} = 0 \quad 1.1.5$$

In free electron approximation, (1.1.5) becomes

$$\epsilon(\vec{k}) = \vec{k}^2 \quad 1.1.6$$

In NFE method the periodic potential can be treated as a perturbation on the free electron states. From (1.1.5), if $\alpha_{\vec{k}} \approx 1$,

we have the approximate solution

$$\alpha_{\vec{k} - \vec{g}} \approx \frac{V_{-\vec{g}}}{\epsilon_{\vec{k}}^0 - \epsilon_{\vec{k}-\vec{g}}^0} \quad 1.1.7$$

where $\epsilon_{\vec{k}}^0 = \vec{k}^2$, etc., and $\epsilon_{\vec{k}}$ can be expanded in second order perturbation

$$\epsilon_{\vec{k}} \sim \epsilon_{\vec{k}}^0 + V_0 + \sum_{\vec{g}} \frac{|V_{\vec{g}}|^2}{\epsilon_{\vec{k}}^0 - \epsilon_{\vec{k}-\vec{g}}^0} \quad 1.1.8$$

But if $\epsilon_{\vec{k}}^0 \approx \epsilon_{\vec{k}-\vec{g}}^0$, this would break down. In one dimensional case

this must occur where $\vec{k} = \vec{k} - \vec{g}$, i.e., at zone boundary ($\frac{1}{2} \vec{G}$).

Here \vec{G} describes a particular reciprocal lattice vector. Suppose that the first term of (1.1.4) and (1.1.5) are considered. After shifting the origin of energy by V_0 , we obtain the determinants with solution

$$\epsilon_{\vec{k}} = \frac{1}{2} (\epsilon_{\vec{k}}^0 + \epsilon_{\vec{k}-\vec{g}}^0) \pm \frac{1}{2} \left\{ (\epsilon_{\vec{k}}^0 - \epsilon_{\vec{k}-\vec{g}}^0)^2 + 4|V_{\vec{g}}|^2 \right\}^{1/2} \quad 1.1.9$$

Thus the behavior of $\epsilon_{\vec{k}}$ in NFE system splits into bands as in Fig 1.2 .

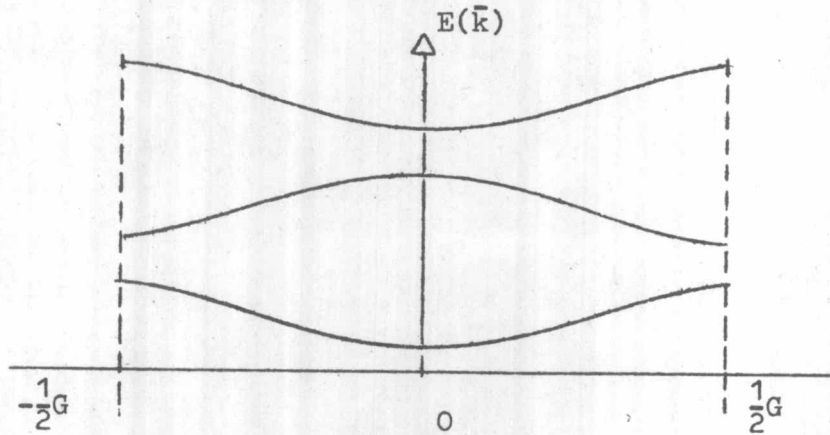


Fig 1.2 Electron energy in one dimension

In order to describe in more details the dispersion relation and the distribution of states in energy in terms of an effective mass tensor, it is more convenient to write the group velocity of an electron wave packet in space as

$$\vec{v} = \frac{1}{\hbar} \nabla_{\vec{k}} E \quad 1.1.10$$

and the acceleration in an external field is

$$\vec{a} = \frac{1}{\hbar} \nabla_{\vec{k}} \left\{ \nabla_{\vec{k}} E \cdot \frac{d\vec{k}}{dt} \right\} \quad 1.1.11$$

If the force on the electron resulting from an external field is \vec{F} , then the time independent Schrödinger equation requires that

$$\vec{F} = - \frac{\hbar d\vec{k}}{dt} \quad 1.1.12$$

Substituting (1.1.12) into (1.1.11), we obtain

$$\vec{a} = -\frac{1}{\hbar^2} \nabla_{\vec{k}} \nabla_{\vec{k}} \vec{E} \cdot \vec{F} \quad 1.1.13$$

Eq. (1.1.13) has the component

$$\vec{a}_i = -\frac{1}{\hbar^2} \sum_j \frac{\partial^2 E}{\partial k_i \partial k_j} F_j \quad \text{etc.}$$

The tensor quantity $\hbar^2 \left\{ \frac{\partial^2 E}{\partial k_i \partial k_j} \right\}^{-1}$ is known as the tensor of

the effective mass with i and j assuming the value of x, y, z

For a coordinate system along the principal axes of the effective

mass tensor, the off diagonal terms vanish. If we let m_x, m_y, m_z

to be the effective mass along the three principal axes then we

obtain $\frac{1}{m_x} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_x^2}$, $\frac{1}{m_y} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_y^2}$, $\frac{1}{m_z} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_z^2}$. If we

consider a spherical constant energy surface in which $m_x = m_y = m_z$, we

obtain a scalar effective mass

$$m^* = \hbar^2 / \frac{\partial^2 E}{\partial k^2}$$

We note that d^2E/dk^2 is positive at the bottom of each band and negative at the top of the band. According to this method, the dependence of E on \vec{k} just above the bottom of the band is to first order of a form

$$E = E_c + \frac{\hbar^2}{2m_c^*} (\vec{k} - \vec{k}_c)^2 \quad 1.1.14$$

where E_c is the energy of the bottom of the band. Similarly near the top of the band

$$E = E_v - \frac{\hbar^2}{2m_v^*} (\vec{k} - \vec{k}_v)^2 \quad 1.1.15$$

To go further we must know the density of states. First we consider the total volume in \vec{k} -space lying between two surfaces of constant energy which are dE apart. This quantity can be expressed as a surface integral $\left\{ \int \frac{dS}{\nabla_{\vec{k}} E} \right\} dE$ and the volume per one electron state is $4(\pi/L)^3$. Thus from the definition we get

$$\rho(E) = \frac{dN(E)}{dE} = \int \frac{dS}{\nabla_{\vec{k}} E} \cdot \frac{1}{4\pi^3} \quad 1.1.16$$

where $N(E)$ is the number of electronic states per unit volume. Eq. (1.1.14) can be differentiated with respect to \vec{k} and set $\vec{k}_c = 0$, to get

$$\frac{dE}{dk} = \hbar^2 k^2 / m_c^* \quad 1.1.17$$

Eq. (1.1.17) can be substituted into (1.1.16) and since $\int ds = 4\pi k^2$ then we obtain

$$\rho_c(E) = 4\pi (2m_c^* / \hbar^2)^{3/2} (E - E_c)^{1/2} \quad 1.1.18$$

Similarly $\rho_v(E) = 4\pi (2m_v^* / \hbar^2)^{3/2} (E - E_v)^{1/2} \quad 1.1.19$

On the other hand we can obtain the density of states from the definition

$$\rho(E) = \frac{1}{\Omega} \sum_{\mathbf{k}} \delta(E - E_{\mathbf{k}}) \quad 1.1.20$$

$$= \frac{1}{\Omega} \cdot \frac{\Omega}{(2\pi)^3} \int_0^{\infty} 4\pi k^2 dk \delta(E - E_{\mathbf{k}}) \quad 1.1.21$$

where $\sum_{\mathbf{k}} = \frac{\Omega}{(2\pi)^3} \int d\vec{k}$. Substituting (1.1.14) into (1.1.21),

we get

$$\rho(E) = \frac{\sqrt{2} m_c^*}{\pi^2 \hbar^3} \cdot \sqrt{E} H(E) \quad 1.1.22$$

where $H(E) = \begin{cases} 0 & E < 0 \\ 1 & E > 0 \end{cases}$

At $T = 0^{\circ}\text{K}$ electrons fill the lowest available energy levels according to Pauli exclusion principle. Since other bands are empty, at $T > 0^{\circ}\text{K}$ some electrons from the highest filled band (valence band) will be thermally excited into the lowest empty band (conduction band) as shown in Fig. 1.3.

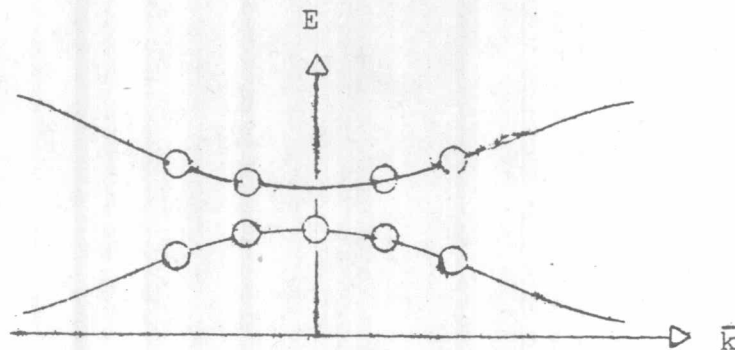


Fig 1.3 The highest fully occupy band and the upper band partially occupied.

In pure semiconductors some electrons in valence band can be thermally excited into the conduction band. Thus they leave behind vacant (empty) states. These electrons occupy the states near the bottom of the conduction band. The vacant states are found in the band maximum. We can describe the electrons in the conduction band as negative charges and the vacant states or holes as positive charges. For many purposes we will not be interested in the shape of energy bands as a function of k so we represent the energy bands in a semiconductor by diagram as shown in Fig 1.4

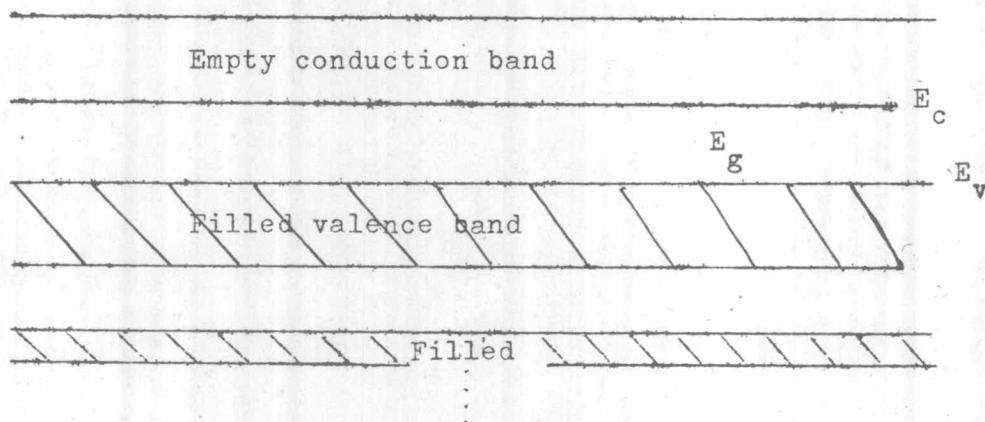


Fig. 1.4 Energy band diagram in pure semiconductor

where E_g is the energy gap or energetic distance between the two bands. The energy distribution of states in crystalline solid is shown in Fig. 1.7.

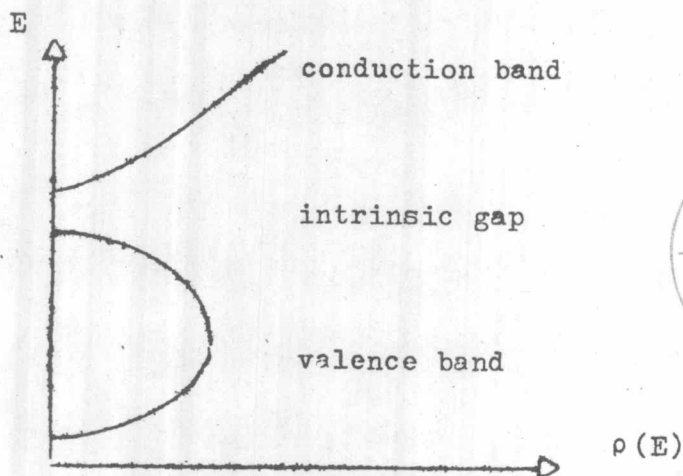


Fig 1.5. Density of states of pure semiconductor (schematically)

1.2 The Shift of Band edge^{9,10}

When we introduce impurities in perfect crystal, they break the periodic structure and changes the properties of materials. An impurity atom may be replaced one of the host atom. It is then called substitutional impurity as shown in Fig. 1.6. Alternatively it may occupy an interstitial site as shown in Fig 1.7.

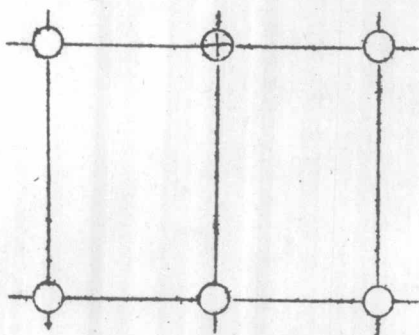


Fig 1.6 Substitutional impurity alloy structure

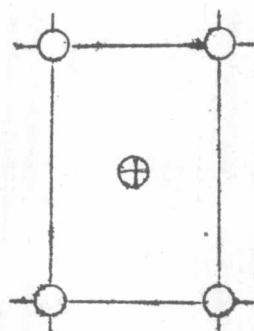


Fig 1.7 Interstitial impurity alloy structure.

As mentioned in Sec. 1.1 the wave functions of all states in perfect crystal are the so called extended states. On the other hand when periodicity is broken, localized states

are allowed and in most cases they appear in the gap. In Wilson's⁵ extreme tight binding model the solid is assumed to be a collection of atoms on periodic lattice and impurity atoms which has a different set of energy levels lie within the energy gap. The model is valid for deep level (the level which $E_I \ll E_g$ where E_I is the ionization energy). For shallow level ($E_I \sim E_g$) the hydrogenic model is appropriate. The latter model can be explained as follows. If we replace one of the host atom by an atom from the column of the periodic table next to the column of the host atom, the impurity atom then has one extra valence electron. If we hold the electron and do not let it enter the crystal, the crystal then has the same valence as it had before i.e., it still has a completely filled valence band and empty conduction band. Since the impurity atom has a positive charge and it contributes an additional coulomb term $u(r) = -\frac{e^2}{\epsilon r}$ where ϵ is the dielectric constant of the medium to the crystal field. Now we let the extra electron go into the system a free electron with mass m^* which is acted on by Coulomb field $e^2/\epsilon r^2$. Like the hydrogen atom, this extra electron has the energy

$$E_n^{(H)} = -\frac{e^4 m^*}{3h^2 \epsilon^2 n^2}$$

We conclude that using the hydrogenic model, the bound states for the electron are below the band edge. As we introduce more impurities to the crystal and assume that the impurities interaction is weak, the electron wave function of neighbouring impurity atoms overlap until they form the impurity band separated from the parent band and the degree of doping is called moderate

doped. When the degree of doping is increased the interaction between impurity atoms increases. The impurity band then merges with the parent band. The degree of doping is now called heavily doped. The influence of heavy doping has been investigated. It is seen that an increase of the impurity concentration, causes a narrowing of the forbidden band. There are also shifts of band edge. Bernstein showed that this phenomena was related to the fact that in heavily doped semiconductor the Fermi level lies above the bottom of the conduction band. This property is similar to metallic hydrogen such as Na etc. Baltenbergers⁹ has used hydrogenic model on semiconductor and Stern¹⁰ has extended the ordinary hydrogenic model of impurities into the range of large impurity concentration by considering in the case of smaller lattice constants. For calculation Baltenbergers set Schrödinger equation of one electron in potential $-e^2/\epsilon r$ and kept periodic interaction in term of effective mass. He assumed that the impurities were arranged in closed pack lattice. The Schrödinger equation is then

$$\frac{\hbar^2}{2m^*} \nabla^2 \psi + \left(\frac{e^2}{\epsilon r} + E \right) \psi = 0 \quad 1.2.1$$

Following Wigner-Seitz method, atomic polyhedra are set up around the impurities. As is clearly seen (1.2.1) is the Schrödinger equation for central force problem. The spherical symmetry of potential energy therefore suggests that one should

work in the spherical co-ordinate system. The solution can be separated in the radial function $R(r)$ and the angular function $Y(\theta, \phi)$, i.e.,

$$\psi = R(r)Y(\theta, \phi) \quad 1.2.2$$

Changing (1.2.1) to spherical co-ordinate and substituting (1.2.2) into (1.2.1), we obtain two equations, i.e., radial part and angular part. The radial equation has the form

$$\left\{ \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{\ell(\ell+1)}{r^2} + \frac{2m^*}{\hbar} \left(\frac{E_{n\ell} + \frac{e^2}{\epsilon r}}{\epsilon r} \right) \right\} R_{n,\ell} = 0$$

1.2.3

where n and ℓ are principal quantum number and angular quantum number respectively. We now define

$$P_{n\ell}(r) = r R_{n\ell}(r) \quad 1.2.4$$

Substituting (1.2.4) into (1.2.2) and we get

$$\frac{\hbar^2}{2m^*} \frac{d^2}{dr^2} P_{n,\ell} - \left\{ \frac{\hbar^2}{2m^*} \frac{\ell(\ell+1)}{r^2} - \frac{e^2}{\epsilon r} - E \right\} P_{n,\ell} = 0 \quad 1.2.5$$

Stern put $r = \left(\frac{\epsilon m}{m} \right) x$ and $E = \left(\frac{m}{m\epsilon} \right) E$ into (1.2.5)

and he obtained for case of $n = 1$,

$$\frac{d^2}{dx^2} P_\ell + \left\{ \frac{2}{x} + E - \frac{\ell(\ell+1)}{x^2} \right\} P_\ell(x) = 0 \quad 1.2.6$$

He obtained solutions of (1.2.6) in three cases.

In case (1) when $E < 0$ the solution is in the form

$$P_{\ell}(x) \sim x^{\ell+1} e^{-x/n} \left\{ 1 + \sum_{i=1}^{\infty} \frac{(\ell+1-n)(2+\ell-n)\dots(i+\ell-n)}{i!(2\ell+2)(2\ell+3)\dots(2\ell+i+1)} \right\} \quad 1.2.7$$

where $n = (-E)^{-1/2}$. In case (2) $E = 0$, he obtained

$$P_{\ell}(x) \sim (8x)^{1/2} J_{2\ell+1}((8x)^{1/2}) \quad 1.2.8$$

where $J_{2\ell+1}$ is a Bessel function of order $2\ell+1$. In case (3)

when $E \gg 0$ he obtained

$$P_{\ell}(x) \sim (x/E)^{1/2} J_{\ell+1/2}(x/E) \quad 1.2.9$$

The energy at the bottom of 1s band E_B can be determined from the Wigner Seitz boundary condition

$$\left. \frac{d}{dx} (x^{-1} P_0(x)) \right|_{x_S} = 0 \quad 1.2.10$$

where x_S is an average distance between impurities. He assumed that in the lower part of the band the energy was approximately given by

$$E(k) = E_B + \alpha^{-1} k^2 \quad 1.2.11$$

where α^{-1} is an effective mass. He also obtained the density of states in the form



$$\rho(E) = \alpha^{-3/2} (E - E_B)^{1/2} / 2\pi \quad 1.2.12$$

He found for the width of the 1s band by considering at $k = 0$

and $k_X = \frac{\pi}{2a}$, i.e., the center and the corner of Brillouin zone,

He obtained

$$\omega = \left(\frac{9\pi}{4}\right)^{2/3} \cdot \alpha x_s^{-2} \quad 1.2.3$$

To calculate α the following equation was used

$$\alpha = \frac{x_s^3 \left\{ P_0(x_s) \right\}^2 \left. \frac{d \left\{ x^{-1} P_1(x) \right\}}{dx} \right|_{x_s}}{3 P_1(x_s) \int_0^{x_s} P_0(x)^2 dx} \quad 1.2.14$$

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Stern chose $E_B < -2$. Then he determined the value of x_s by using (1.2.10). Substituting the chosen value E_B and the computed value x_s into (1.2.7) and letting $l = 0$, he obtained the value of $P_0(x)$. To solve the value of α he replaced the previous value of $P_0(x)$ and x_s in (1.2.14). By substituting the computed value α into (1.2.13), the value of ω can be obtained. The above procedure was repeated and he collected the values of E_B , α and f where f was the position of the fermi level at absolute zero temperature and which is given by $f = E_B + \omega$.

From these values, he noticed that as the lattice constant decreased, the Fermi level rose much more rapidly than the bottom of the band fell. Here he used the relation $\frac{4}{3} \pi x_s^3 = \frac{1}{N_D}$

where N_D is donor concentrations and transformed E_B and f in suitable unit. He plotted the graph for the energy versus N_D as shown in Fig 1.8 which showed that the more doping concentration the more separation between f and E_B .

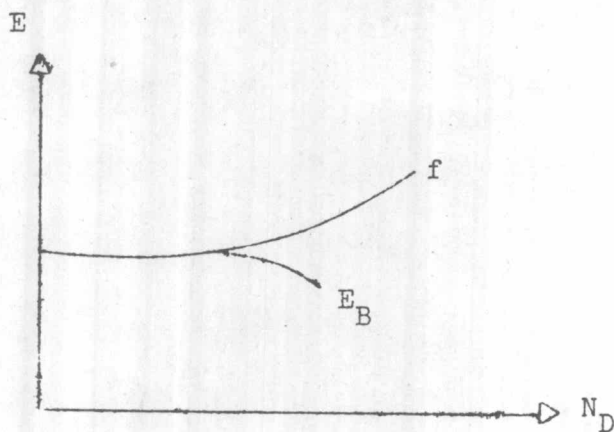


Fig 1.8 The theoretical Fermi level (the top curve) and the energy of the bottom of 1s impurity band (the bottom curve)

The hydrogenic model shows that in heavily doped limit the impurity band merges with the parent band.

In conclusion Stern suggested that the most serious objection to the calculation is that the neglect of randomness. The work of James and Ginzberg and of Aigrain and Jancovici has shown that when impurities are randomly distributed there will be a tail in the density of states at both edges of the band.

1.3 The Virtual Crystal Approximation.¹²

When a semiconductor is heavily doped, the main effects are (i) a shift of band edge and (ii) band tailing.

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Wolff showed that the shift of band edge is due to the exchange energy while the band tailing arises from random nature of impurity sites. We have considered less than ideal crystal since the lattice sites are occupied by the impurity in a random nature.

An example is the disordered semiconductor alloy $A_x B_{1-x}$. The one-electron Hamiltonian is

$$H = \frac{-\hbar^2 \nabla^2}{2m^*} + V(\vec{r}) \quad 1.3.1$$

where

$$V(\vec{r}) = \sum_{\ell} \frac{1}{2} \left\{ V^A(\vec{r}-\vec{R}_{\ell}) + V^B(\vec{r}-\vec{R}_{\ell}) + \alpha(\vec{R}_{\ell}) \right. \\ \left. (V^A(\vec{r}-\vec{R}_{\ell}) - V^B(\vec{r}-\vec{R}_{\ell})) \right\} \quad 1.3.2$$

Here V^A and V^B are the potential of atoms of type A and type B.

$\alpha(\vec{R}_{\ell})$ is the random number and \vec{R}_{ℓ} is the center of the atom. In disordered system we cannot use Bloch's theorem. The problem becomes a statistical one which gives some kind of configuration averaging. The problem can only be solved approximately. In this section we mention about the earliest model which considers the effect of randomness as perturbation of periodic system: the virtual crystal approximation. This method consists of replacing the real potential centered on each lattice site by an averaged crystal potential, the potential is formed by averaging potential V^A and V^B , so that we have

$$V^{VC}(\bar{r} - R_l) = \langle V \rangle = XV^A + (1-X)V^B \quad 1.3.3$$

where $\langle \quad \rangle$ denotes the average, X is fraction of atoms of type A. The above is a good approximation only if V^A and V^B do not differ too much the corresponding Hamiltonian becomes

$$H_0 = \frac{\hbar^2 \nabla^2}{2m^*} + \langle V \rangle \quad 1.3.4$$

With the above equation V.C.A may be considered as a starting approximation. We note that H_0 is periodic with the period of crystal lattice. So (1.3.4) can be calculated as the same way as the case of perfect crystal. This approximation yields a solution which looks like that of a perfect crystal with a simple shift $\langle V \rangle$. The solution becomes exact for small perturbation V . For this case the perturbed wave function are quite extended in space and each particle therefore sees the average perturbation. From (1.3.4) we can rewrite (1.3.1) in the following form

$$\begin{aligned} H &= H_0 + V(\bar{r}) - \langle V \rangle \\ &= H_0 + U \end{aligned} \quad 1.3.5$$

To solve (1.3.5), we treat U as a perturbation potential. The solution shows that the lack of periodic causes a tailing of the density of states in the neighborhood of the band edges into the forbidden gap. We note that the VCA approximation is

the lowest order term in a perturbation series and may be extended by including more terms.

1.4 The Effect of Second Order Perturbation^{3,13}

Parmenter applied the perturbation method to the alloy problem. He used the VCA by choosing virtual crystal potential to be unperturbed potential. The corresponding Hamiltonian is

$$H = H_0 + \sum_i V(\vec{r} - \vec{R}_i) \quad 1.4.1$$

where H_0 is unperturbed Hamiltonian, $V(\vec{r} - \vec{R}_i)$ represents the potential of a single impurity at position \vec{R}_i . He averaged (1.4.1) over all configurations. By assuming coherent scattering, the Schrodinger equation becomes

$$H \psi(\vec{k}, \vec{r}) = \left\{ H_0 + \sum_i V(\vec{r}) \right\} \psi(\vec{k}, \vec{r}) \quad 1.4.2$$

where H_0 satisfy the relation

$$H_0 \psi_0(\vec{k}, \vec{r}) = E_0(\vec{k}) \psi_0(\vec{k}, \vec{r}) \quad 1.4.3$$

If we assume the solution to be normalized plane wave

$$\langle \vec{r} | \vec{k} \rangle = \psi_0(\vec{k}, \vec{r}) = \Omega^{-1/2} e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}} \quad 1.4.4$$

we get

$$E_0(\vec{k}) = \epsilon + \frac{\hbar^2}{2m^*} (k - k_0)^2 \quad 1.4.5$$

$V_i(\vec{r})$ is now taken to be the form of screened coulomb potential

$$V_i(\vec{r}) = \frac{z_i e^2}{\epsilon_d} \frac{\exp(-Q|\vec{r} - \vec{R}|)}{|\vec{r} - \vec{R}|} \quad 1.4.6$$

and letting it be the perturbing potential where Q is a reciprocal screening length, $z_i e$ is the electronic charge of impurity center at \vec{R} , and ϵ_d is the dielectric constant. By using perturbation technique we expand (1.4.2) to second order and obtain

$$E(\vec{k}) = E_0(\vec{k}) + \sum_i N_i \langle \vec{k} | V_i | \vec{k} \rangle + \sum_i N_i \sum_{k \neq k} \frac{\langle \vec{k} | V_i | \vec{k} \rangle^2}{E_0(\vec{k}) - E_0(\vec{k})} \quad 1.4.7$$

We consider

$$\begin{aligned} \langle \vec{k} | V_i | \vec{k} \rangle &= \int \psi_{\vec{k}}^* V_i \psi_{\vec{k}} d\vec{r} \\ &= \frac{1}{\Omega} \int_0^{\infty} v(\vec{r}) d\vec{r} \\ &= \frac{4\pi}{Q^2} \left(\frac{-ze^2}{\epsilon_d} \right) \end{aligned}$$

Therefore

$$\sum_i N_i \langle \vec{k} | V_i | \vec{k} \rangle = \frac{4\pi}{Q^2} \sum_i \frac{N_i}{\Omega} \left(\frac{-ze^2}{\epsilon_d} \right) = E_1 \quad 1.4.8$$

We can define $n_i = \frac{N_i}{\Omega}$ as the concentration per unit volume.

We now consider

$$\begin{aligned}
 \langle \vec{k}' | V_i(\vec{r}) | \vec{k} \rangle &= \int \psi_{\vec{k}'}^* V_i(\vec{r}) \psi_{\vec{k}} d\vec{r} \\
 &= V_i(\vec{k}) \\
 &= -\frac{4\pi}{(Q^2 + (k-k_0)^2)} \cdot \frac{ze^2}{\epsilon_d} \quad 1.4.9
 \end{aligned}$$

$$\text{and} \quad E_0(\vec{k}) - E_0(\vec{k}') = \frac{\hbar^2}{2m^*} ((k-k_0)^2 - (k'-k_0)^2)$$

Let $\vec{k}-\vec{k}_0 = \vec{k}_i$ and $\vec{k}'-\vec{k}_0 = \vec{k}_j$. Since k is a dummy variable, thus we can substitute \vec{k}_j by $\vec{k}_i - \vec{k}_j$. So

$$E_0(\vec{k}) - E_0(\vec{k}') = \frac{\hbar^2}{2m^*} (2\vec{k}_i \cdot \vec{k}_j - k_j^2) \quad 1.4.10$$

Substituting (1.4.8), (1.4.9), and (1.4.10) into (1.4.7) and

changing $\frac{\Sigma}{k}$ to $\frac{\Omega}{2\pi^3} \int d\vec{k}$, (1.4.7) can be integrated over

all space. By changing k_j to σ and using the residue

theorem, we have

$$\left\{ \left\{ Q^2 + \sigma^2 \right\}^{-2} \left\{ \sigma \cdot (2k - \sigma) \right\}^{-1} d\zeta_\sigma \right\} = -\frac{(\pi^2)}{Q} (Q^2 + 4k^2)^{-1}$$

Thus

$$E_2(\vec{k}) = \sum_i N_i \sum_{\vec{k} \neq \vec{k}'} \frac{|\langle \vec{k} | V_i(\vec{r}) | \vec{k}' \rangle|^2}{E_0(\vec{k}) - E_0(\vec{k}')} = \frac{2\pi}{Q} \sum_i \frac{N_i}{\Omega} \left(\frac{-ze^2}{\epsilon_d} \right)^2 \frac{\hbar^2}{2m^*} (Q^2 + 4(k-k_0)^2)$$

1.4.11

Using (1.4.5), (1.4.7), (1.4.8) and (1.4.11) we can find k in terms of E , i.e.,

$$2(k - k_0)^2 = (E - E_c - \frac{1}{4}E_Q) + \left\{ (E - E_c + 1/4E_Q)^2 + \xi \right\}^{1/2}$$

1.4.12

where $E_c = \epsilon + E_0$, $\xi = \frac{2\pi}{Q} \sum_i n_i \left(\frac{-ze^2}{\epsilon_d} \right)^2$ and $E_Q = \frac{\hbar^2 Q^2}{2m^*}$

From the definition $\rho(E) = \frac{dn'}{dE} = \frac{dn'}{d(k-k_0)} \cdot \frac{d(k-k_0)}{dE}$ 1.4.13

where n' is the total number of states per unit volume having an energy less than $E(\vec{k})$ and

$$n' = \frac{N}{\Omega} = (k - k_0)^3 / 6\pi^2$$
 1.4.14

We obtain

$$\begin{aligned} \rho_p(E) &= \frac{1}{\pi^2} (k-k_0)^2 \frac{d(k-k_0)}{dE} \\ &= \frac{1}{2\pi^2} \frac{Q^3}{(2E_Q)^{3/2}} \left\{ (E-E_c) - \frac{1}{4}E_Q + \left[\left\{ (E-E_c) + \frac{1}{4}E_Q \right\}^2 + \xi \right]^{1/2} \right\}^{1/2} \\ &\cdot \left[1 + \left\{ (E-E_c) + \frac{1}{4}E_Q \right\} \left(\left\{ (E-E_c) + \frac{1}{4}E_Q \right\}^2 + \xi \right)^{-1/2} \right] \end{aligned}$$
 1.4.15

$\rho(E)$ shows the sharp cut off in the tail state. Parmenter expanded (1.4.7) to higher order but still found the cut off to be sharp.

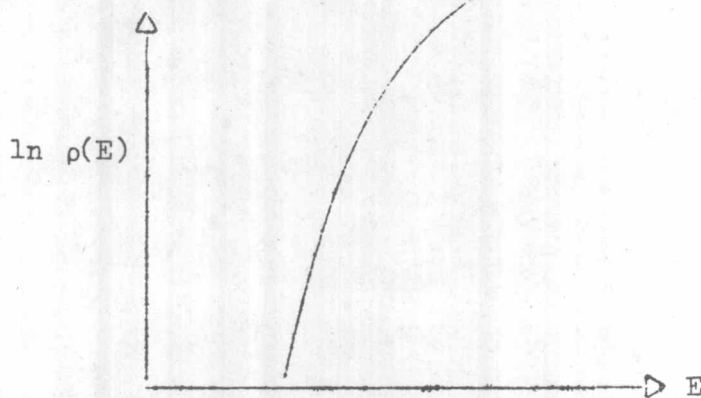


Fig 1.9 The density of states calculated from second order perturbation method (schematically)

1.5 Coherent Potential Approximation (CPA) ^{8,12,14,15}

The method was introduced by Soven for the study of electrons in substitutional alloy. It arises from a self consistent solution of multiple scattering expansion of the Schrödinger equation within a single site approximation in which the properties of all sites but one are averaged over. The remaining one is treated exactly. It is useful in description of short range scattering in the alloy. It can be extended by extrapolating away from the limits of low concentration and weak scattering. The CPA is based on a non degenerate tight binding band. The effective Hamiltonian describes an averaged system which contains a scattering contribution of two components

$$H = W + \sum_n D_n$$

where W is a periodic part and D is the sum of random contribution. The one electron properties of the alloy are given as an ensemble averaged over all possible arrangements of the Green's function

$$\begin{aligned} \langle G(Z) \rangle &= \langle (Z-D-W)^{-1} \rangle \\ &= (Z-W-\Sigma)^{-1} \end{aligned} \quad 1.5.2$$

where z is complex energy.

If the T matrix for a given configuration is defined by

$$\langle G \rangle = \langle G \rangle + \langle G \rangle T \langle G \rangle \quad 1.5.3$$

then

$$T = V + V \langle G \rangle T$$

To determine Σ , we use a self consistent condition for the choice of Σ , i.e.,

$$\langle T \rangle = 0 \quad 1.5.4$$

We can define

$$D - \Sigma = \sum_n (D_n - \Sigma) = \sum_n V_n \quad 1.5.5$$

where $\sum_n V_n$ is the perturbing random potential. The T

matrix for the site n is defined by

$$\langle T_n \rangle = V_n (1 - \langle G \rangle V_n)^{-1} \quad 1.5.6$$

where

$$T = \sum_n T_n$$



Eq(1.5.4) describes the effect of replacing the effective medium which is characterized by Σ by the true atom at the given site n as shown in Fig 1.10. The C.P.A. replaces the general self-consistently condition (1.5.4) by

$$\langle T_n \rangle = 0 \quad 1.5.7$$

which means that the average effect of substituting true atom at a given site in the effective crystal is zero. From (1.5.2) we can write

$$\langle G \rangle = G^0(Z - \Sigma(Z)) \quad 1.5.8$$

where $G^0(Z) = (Z - W)^{-1}$ is the unperturbed Green's function. Next one can write

$$V_n = \epsilon_n - \Sigma(Z) \quad 1.5.9$$

If we define

$$F(Z) = \langle n | \langle G \rangle | n \rangle = \frac{1}{N} \text{Tr} \langle G \rangle \quad 1.5.10$$

and

$$F^0(Z) = \langle n | G^0(Z) | n \rangle = \frac{1}{N} \text{Tr} G^0(Z) \quad 1.5.11$$

We can write

$$F(Z) = F^0(Z - \Sigma) \quad 1.5.12$$

Substituting (1.5.9) into (1.5.6) and use (1.5.10), we get

$$T_n = (\epsilon_n - \Sigma(Z)) \left\{ 1 - \frac{[\epsilon_n - \Sigma(Z)]}{\epsilon_n - \Sigma(Z)} \cdot F(Z) \right\}^{-1} \quad 1.5.13$$

Using (1.5.7) and (1.5.13) we can solve Σ . As an example we consider in the case of binary alloy $A_x B_y$. There we obtain

$$\Sigma(Z) = \epsilon + (\Sigma - \epsilon^A) F(Z) (\Sigma - \epsilon^B) \quad 1.5.14$$

where ϵ^A is an energy of atom at site A and ϵ^B is an energy of atom at site B. Since

$$\epsilon = \langle\langle 0|D|0 \rangle\rangle = x\epsilon^A + y\epsilon^B = x\epsilon^A + (1-x)\epsilon^B \quad 1.5.15$$

Eq. (1.5.11) can be rewritten as

$$F^0(Z) = \int_{-\infty}^{\infty} \frac{dE}{Z-E} \rho^0(E) \quad 1.5.16$$

where $\rho^0(E)$ is the density of states of an unperturbed crystal.

In tight binding approximation $\rho^0(E)$ can be written in the form

$$\rho^0(E) = \frac{-1}{\pi} \text{Im} F^0(Z) = \frac{1}{N} \sum_k \frac{1}{z - S(k)} \quad 1.5.17$$

and

$$\rho(E) = \frac{-1}{\pi} \text{Im} F(Z) = \frac{-1}{\pi} \text{Im} F(E + i0) \quad 1.5.18$$

By iteration techniques, the value of Σ can be solved from (1.5.14). Then by solving (1.5.14) and (1.5.12) self consistently by computer, and using (1.5.18) we obtain the value of $\rho(E)$. The graph of $\rho(E)$ versus E is shown in Fig 1.11. The density of states lacks the tail corresponding to localized states.

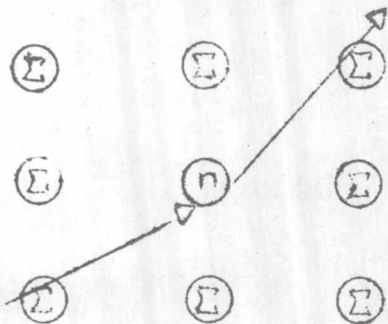


Fig 1.10 Model of CPA

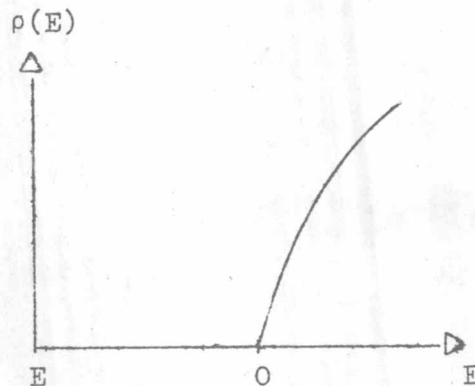


Fig 1.11 The density of states calculated from CPA method (schematically)

1.6 Edwards' Formalism ^{8,16,17}

Edwards has developed a method for calculating the density of electron states in a liquid in which the core potential is weak. He worked with a 1 - dimensional and completely disordered system. The corresponding Schrödinger equation can be written as

$$(E + \nabla^2 + \sum_{\alpha} v(r - R_{\alpha}) + i\epsilon) G(x, x') = \delta(x - x') \quad 1.6.1$$

where $v(r - R_{\alpha})$ is the weak scattering potential at R_{α} . Edwards expressed G which is in momentum representation in terms of its

Dyson's equation

$$G(k) = G_0(k) - G_0(k) V G(k) \quad 1.6.2$$

where

$$G(k) = \frac{1}{\Omega} \int e^{-ik \cdot (x-x')} G(x, x') dx dx' \quad 1.6.3$$

and V is the deviation of potential from its mean. Then G can be averaged by considering its expansion in terms of V . Therefore we obtain

$$\begin{aligned} \langle G \rangle &= G_0(k) - G_0(k) \langle V \rangle \langle G \rangle \\ &= G_0(k) - G_0(k) \langle V \rangle G_0(k) \\ &\quad + G_0(k) \langle V \rangle G_0(k) \langle V \rangle G_0(k) + \dots \end{aligned} \quad 1.6.4$$

where $G_0(k) = (E - k^2 + \langle V \rangle + i\epsilon)^{-1}$ is the unperturbed Green's function and $\langle V \rangle$ is an average potential, which is defined by $\langle V \rangle = \langle V - \langle V \rangle \rangle$ with V being the atomic potential. Edwards considered the case of a delta function potential. For this case $V(k)$ can be written in the form

$$V = \lambda \left(\frac{L}{N} \right)^{1/2} \quad 1.6.5$$

where N is the number of scattering center and L is the total volume. He kept only the terms involving VV , VVV ...

In the completely disordered case he found

$$\langle G \rangle = (E - k^2 + i\Gamma)^{-1} \quad 1.6.6$$

where $\Gamma = \pi N^2 / 2 \sqrt{E}$

By definition the spectral density of state is

$$\rho(k, E) = \frac{-\text{Im} \langle G(k) \rangle}{\pi} \quad 1.6.7$$

If we substitute (1.6.6) into (1.6.7), we obtain

$$\rho(k, E) = \Gamma ((E - k^2)^2 + \Gamma^2)^{-1} \quad 1.6.8$$

Using (1.6.8) the density of states is obtained

$$\begin{aligned} \rho(E) &= \int_{-\infty}^{\infty} \rho(k, E) dk \\ &= \pi^2 \sqrt{\Gamma - E} \end{aligned} \quad 1.6.9$$

The 1-dimensional density of states shows the tail that cut-off sharply as is shown in Fig. 1.12

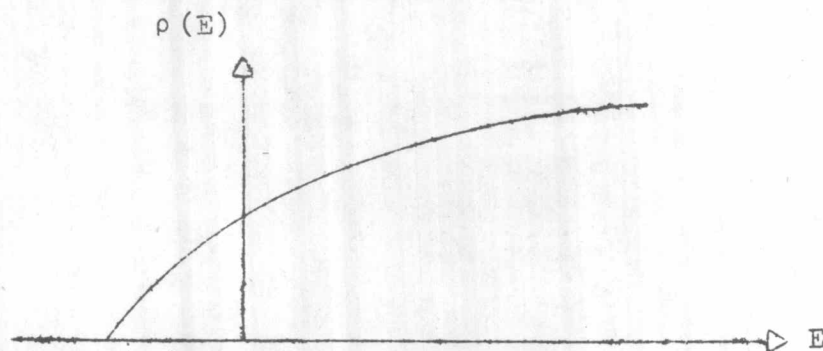


Fig 1.12 Density of states calculated from Edwards' formalism (schematically).

The theory of impurity band density of states in the heavily doped semiconductor has passed through several stages : section 1.2 - 1.6. It does not agree with some experiments on tunneling, optical absorption and luminescence which give evidence for an exponential tail. This failure shows the inadequacy of perturbative methods in predicting the behavior of the tail. Lifshitz¹⁸ proposed that the tail of energy band arose from fluctuations of potential energy. The successive nonperturbative techniques will be shown in the next chapters. In chapter II, III and IV the semiclassical method and quantum method will be shown respectively. In chapter V the Lloyd and Best variational principle will be introduced and used to find the best choice of the density of states.