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A THEORETICAL STUDY OF ELECTRONIC PROCESSES
IN
POLAR SEMICONDUCTORS

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BY

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SYNOPSIS

The thesis comprises four chapters. The first chapter is devoted to the study of the general solid state theory, wherein we have reviewed the dynamics of the charge carriers, their statistical distribution among the available quantum states and their scattering mechanisms. In these discussions, we have focussed our attention to semiconductors.

In chapter 2, we consider the electronic motion in polar semiconductors and their solid solutions. The systems chosen for the study are Lead Chalcogenides (PbX group where X is S, Se or Te). From the physical properties of the PbS group reviewed by Scanlon the important points to note are (i) the high mobility, (ii) that the mobility seems to be independent of the nature and concentration of the carriers, (iii) the temperature dependence of the mobility is of the form $\mu = \mu_0 T^{-n}$, where n = 2.5 and this behaviour is observed for a wide temperature range from about 80°K to 500°K, (iv) the solid solutions of the PbS group exist in all proportions and the mobility of the charge carriers in solid solutions depends on the concentration of one of the components of the alloy and on temperature.

After reviewing the earlier theories of mobility in polar semiconductors and noting their inadequacy, we have introduced new concepts such as multiband conduction in

this chapter. It is envisaged that the inter-band transition of the charge carrier may play an important role in the mobility problem of the polar semiconductor. Such transitions are assisted by the lattice vibrational modes in the case of pure compounds and by the perturbing alloy potential in solid solutions.

In chapter 3, the interaction Hamiltonian has been formulated keeping in mind the aforementioned concepts, namely, the multiband conduction for the following two cases.

Case 1. Pure Compound:- The optical or polar modes in the reststrahlen region are assumed to be important in effecting an inter-band transition and both acoustic and optical modes are taken into account for the scattering of the charge carriers. It is found that the two-phonon processes are important for the transport problem in the high temperature region.

Case 2. Solid Solution:- In the case of solid solutions additional perturbations arising out of alloying effects are assumed to cause inter-band transition and the acoustic modes of lattice vibration scatters the charge carriers. It is found that the one phonon scattering processes coupled with the modifications of the state functions by alloying effect are important in the mobility problem of the solid solutions.

The relaxation times and thereby the mobility expressions are obtained by solving the well/known Boltzmann transport equation. In the first case the mobility versus temperature relation is of the form $\mu = \mu_o T^{-5/2}$ in the high temperature region ($T > \theta$; θ being the characteristic temperature).

For the case 2 the mobility expression in the low temperature region ($T > 50°K$) is of the form $\mu = \mu_o^{(s)} T^{-3/2}$ where $\mu_o^{(s)}$ is a function of the concentration of the components and it is given by

$$\mu_o^{(s)} = \frac{a}{b + 2\xi_{d'}^2 \sum\limits_{r,s} f_r \, f_s \, |F_{rs}|^2}$$

Here a, b are constants; f_r and f_s being the concentrations of the components (r and s) of the solid solutions.

A resultant mobility expression has been obtained by addition of reciprocal mobilities of the two cases mentioned above.

In chapter 4 we have given a discussion of the two models, namely, continuum model and atomistic model which have been utilised in chapter 3. Based on these two models, the order of magnitude of the mobility has been discussed for the case 1.

It is concluded that the temperature dependence as well as the order of magnitude of the mobility of the charge carriers are in very good agreement with the observed data.

In the case 2, we have compared the theory given in chapter 3 with the experimental results on the PbTe - PbSe system. The constants a and b were determined from the experimental graph of Joffe and collaborators. It is shown that there is a close agreement between the experimental data and the theoretical curve for the mobility - concentration dependence.

It is concluded that the inter-band transition effects in the polar semiconductors, whether caused by optical phonons or alloying perturbation do indeed play an important role in the transport problem.

CHAPTER - 1

GENERAL INTRODUCTION

A. CHARGE CARRIERS: (Electrons and Holes)

In this chapter, the behaviour of electrons in crystalline solids in general and semiconductors in particular is considered.

In order to understand the various phenomena such as electrical and thermal conductivities etc. of solids, it is necessary to consider the class of elementary carriers of energy and charge namely electrons or holes. The electronic configuration of an atom consists of closed shells of electrons as well as valence electrons. It is known that only those valence electrons which are free to move in a solid are responsible for the conduction of heat and electricity.

Drudé[1] in 1900 gave the free electron gas theory for a metal based on the principles of classical kinetic theory of gases. Later Lorentz[2] improved the theory by taking into account the statistical nature (Maxwell-Boltzmann Statistics) of the electrons. A wave mechanical free electron theory for metals was developed by Sommerfeld[3] in 1928 on the assumption that a valence electron moves freely throughout the volume of the crystal in an average constant potential due to the rest of the valence electrons and ion cores. The theory, though crude, was able to explain many of the experimental facts approximately. However, with this model it is difficult to understand as to why some of the crystalline solids are good conductors and others are insulators and semiconductors. This difficulty was removed by considering the periodic nature of the potential of ion cores in which the electron is moving.[4,5] This leads to the band picture of solids. The atomic states of the electron of the isolated atoms spread into allowed regions of energy separated by forbidden regions because of the interaction of the ion cores with the electrons. The lower atomic like states spread into narrower band compared to the higher ones. The various quantum states of the bands are filled by the electrons according to the Fermi-Dirac distribution which can be written as

$$f(E) = \frac{1}{e^{(E-\zeta)/k_B T} + 1} \tag{1.1}$$

The highest filled band is called valence band and the first incomplete band is called the conduction band. In general these two bands are separated by a forbidden region of energy called forbidden gap. But in metals the two bands may overlap, thereby conduction electron can be found in the band participating in the conduction processes even at very low temperature. Let us consider an insulator and a semiconductor. In the case of semiconductors the gap is of the order of one electron volt and hence, electrons can be thermally excited from valence band to conduction band to participate in the conduction processes. In the case of insulators thermal excitation of electrons is negligible owing to the large band gap, and electron conduction phenomena will not occur even at high temperatures. This is the model of a solid proposed by Wilson[4] in 1931. When an electron goes to a conduction band the vacancy in the valence band may be considered as a particle called a hole. This hole whose charge is equal and opposite to that of an electron, moves in the opposite direction to that of an electron. Hence, the motion of the holes contributes to the hole conduction. These are the two particles one deals with in a semiconductor theory and a study of the behaviour of these particles in a semiconductor is of vital importance for the transport processes.

B. MOTION OF CHARGE CARRIERS IN A PERFECT CRYSTAL

It is difficult to determine the motion of all the charge carriers in a perfect crystal. This is because of the fact that both the valence electrons and the atomic nuclei are in motion at any finite temperature. Some simplifying assumptions are necessary to solve the problem and one such approach is that of "Adiabatic approximation". With its help the problem can be reduced to one involving a single electron. On this approach the one electron under consideration is supposed to move in the field of the atomic nuclei and all the other electrons, averaged in a suitable manner over the motions of these charges. Further, it is assumed that the field in which the one electron is moving has the same kind of periodicity and symmetry as the crystal lattice and it can be represented by

$$V(\underline{r}) = V(\underline{r} + \underline{d}) \qquad (1.2)$$

where $\underline{r}$ is the position vector of the one electron and $\underline{d}$ being the lattice vector.* The motion of the electron in the periodic lattice potential $V(\underline{r})$ is described by the one electron Schrondinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left\{E - V(\underline{r})\right\}\psi_{\underline{k}t} = 0 \qquad (1.3)$$

Bloch[7] in (1928) demonstrated that the solution of the equation (1.3) can be written in the form

$$\psi_{\underline{k}t} = e^{i\,\underline{k}\,\underline{r}}\;U_{\underline{k}t}(\underline{r}) \qquad (1.4)$$

now known as Bloch states. Here $\underline{k}$ is a vector of the

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[*] $d = d_1\underline{a}_1 + d_2\underline{a}_2 + d_3\underline{a}_3$. Here $\underline{a}_1$, $\underline{a}_2$ and $\underline{a}_3$ are three fixed vectors called basic vectors. d_1, d_2 and d_3 are integers. The space described by these triad of vectors is called a direct space in which the crystal lattice is defined.

reciprocal space[*] and $U_{\underline{k}t}(\underline{r})$ is the function having the periodicity of the lattice. It can be shown using the translation periodicity of the lattice that $\underline{k}$ is the wave vector of the electron and t is the band index. Also every state of the electron has its wave vector. It is evident from the property of the Bloch functions that the wave vectors for the electronic states are arbitrary upto the addition of the vectors of the reciprocal lattice and it is represented by $\underline{k}' = \underline{k} + \underline{g}$ where $\underline{g}$ is the reciprocal lattice vector. Any $\underline{k}$ vector lying outside the first Brillouin zone[**] can be brought inside the first zone by selecting a suitable reciprocal lattice vector. The energy function of the electron is periodic in $\underline{k}$ and when all the $\underline{k}$ values are brought to the central or first zone, we have what is known as reduced

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[*] It is convenient to think of a space called reciprocal space described by a triad of basic vectors $\underline{b}_1$, $\underline{b}_2$ and $\underline{b}_3$ which are defined by the following relations:

$$b_1 = \frac{\underline{a}_2 \times \underline{a}_3}{\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3}\ , \quad b_2 = \frac{\underline{a}_3 \times \underline{a}_1}{\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3}\ , \quad b_3 = \frac{\underline{a}_1 \times \underline{a}_2}{\underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3}$$

In the reciprocal space we define a vector $g = g_1\underline{b}_1 + g_2\underline{b}_2 + g_2\underline{b}_3$ known as reciprocal lattice vector which describes a reciprocal lattice. Here g_1, g_2 and g_3 are integers.

[**] The reciprocal space can be divided into different regions called Brillouin zones, inside each of which the energy is a continuous function of the wave vector, $\underline{k}$. The region about the origin of the reciprocal lattice is called the central zone or first Brillouin zone.

zone scheme.[5] The energy $E_{\underline{k}t}$ in the reduced zone scheme is multivalued and separates into branches or bands. A knowledge of only one branch of multivalued function $E_{\underline{k}t}$ is sufficient for finding the form of the energy band.

The number of states in a band is just the number of $\underline{k}$ values in the first Brillouin zone, which is equal to the total number of unit cells in the crystal.[5] Each $\underline{k}$ state can accommodate two electrons of opposite spins. Further, the factor $N(E)dE$ ($N(E)$ being the density of states), which is the number of states contained between the energy range E and $E + dE$, gives a quantitative representation of the band scheme. Another important concept which is very useful is the Fermi energy. In general this can be defined as that energy which separates the occupied and unoccupied region of energy, by electrons in k-space. In the case of pure semiconductors mathematically one can visualise from expression (1.1) as that energy for which the occupational probability is half. Thus in the case of pure semiconductors the Fermi level E_F lies in the middle of the forbidden gap and for an impurity semiconductor its position is decided by the impurity level, the temperature and the distribution function. To know the form of the band one has to solve the appropriate wave equation for the electron and obtain the E versus $\underline{k}$ relation.[8] The relation of the form[5]

$$E = \frac{\hbar^2 k^2}{2m^*} \qquad (1.5)$$

describes what is known as a parabolic band with m^* as the effective mass of the electron. This gives rise to constant spherical energy surfaces in <u>k</u> space. This is the simplest form that one can have for the energy band. However, semiconductors do not possess such a simple band structure and it is only a simplifying assumption. All the real semiconductors exhibit a complicated band structure, such as ellipsoidal or spheroidal surfaces of constant energy.[6] For all transport problems in semiconductors one is interested near the band extrema, namely, the conduction band minimum or the valence band maximum. In the simple band model discussed above both the band extrema occur at $\underline{k} = 0$ and an electron can undergo a direct transition from valence band maximum to the conduction band minimum, with the help of thermal or optical energy. Generally, in semiconductors these band extrema do not occur at the same value of <u>k</u> but at different <u>k</u> values. Hence the direct transition indicated above is not the only process, but indirect transitions may also occur.[6]

It is clear from what has been said above that the study of the band structure of a semiconductor is of great importance, which helps us to understand the transport mechanism of charge carriers. The parameters that are to be determined from band structure calculations are the energy gap E_g, the position of band extrema in <u>k</u>-space, the effective mass of the electrons and the holes, and finally the form of the E vs <u>k</u> curve. Once these parameters are determined, one can deduce the nature of the band i.e. whether it is nondegenerate, degenerate, simple or multiply connected.

The mass of the electron in a crystal lattice is always something different from the free electron mass of an isolated atom. In this context the actual mass of the electron in the periodic potential of the crystal lattice is defined as an effective mass of the electron and it arises due to the dynamics of the electron in a periodic potential. In the simple band model of constant spherical energy surface, we have for the reciprocal effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E}{\partial k^2}\right) \tag{1.6}$$

In the case of a complicated band structure, the most general relation for reciprocal effective mass can be written in the form[5]

$$\frac{1}{m^*_{rs}} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E}{\partial k_r \, \partial k_s}\right) \tag{1.7}$$

Thus for a complicated band structure the effective mass parameter is a tensor and for a simple band structure, the expression (1.7) reduces to (1.6) which is a scalar quantity.

The expression for the density of state function N(E) defined earlier can be written in the form

$$N(E) = \frac{V}{(2\pi)^3}\,\frac{d}{dE}\int d^3\underline{k} \tag{1.8}$$

Here, the integral is to be taken over the volume of the k-space bounded by a surface of constant energy E.

The energy gap E_g can be determined from the thermal or the optical measurements. The calculation of the band structure is really a difficult task as it involves tedious computations. There exist excellent review articles[9,10,11] where the subject is dealt with from various points of view. In any band structure calculation one will depend heavily on the group theoretical methods and the conclusions drawn from such a calculation is of great value in the scattering mechanisms of charge carriers to be discussed later in this chapter.

It is a general procedure in a band structure calculation[8] to assume that the one electron potential is known and hence the one-electron solution. Then the problem is solved by determining the crystal field potential in the Hartree-Fock approximation. The problem of band structure is essentially a problem of solving the one-electron equation (1.3) under the various methods of finding the solution $\psi_{\underline{k}t}$. They all involve expansion of the unknown function in sets of known functions namely, plane waves, products of radial functions and spherical harmonics, solution of atomic self-consistent field problem etc. In each method of band structure calculation the boundary conditions and the remaining requirements on the wave functions are different.

Wigner and Seitz[12] in 1933 developed a method of calculating the band structure now known as the cellular method. The essential feature of this method is extremely simple. The Schrodinger equation for the one electron is solved in one atomic cell subject to the boundary conditions on the wave function and its derivitive which can be obtained by Bloch's theorem. It is also assumed that the crystal field potential is spherically symmetrical in any given polyhedral cell. This method has been used in the band structure calculation of PbS semiconductor by Bell et al[13] in 1954.

Another method of interest is that due to Bloch[7] in 1928, the so called tight-binding method, where the free atomic states were used to construct the Bloch states. It is to be noted that the tight-binding method applies to electrons that are tightly bound to their own atoms, such as d-electrons in the transition metals. However, Parmenter[14] and Raimes[15] have discussed the inadequacy of the method for valence electrons in metals. The difficulty with the tight-binding method is that we are trying to represent a state of the electron in the crystal environment in terms of free atomic states.

There are other approaches wherein better functions are constructed to satisfy more realistic conditions that one comes across in a crystal lattice. These functions are combinations of plane waves with appropriate boundary conditions to suit the physical situations. These are the wellknown methods of plane wave. Herring[16] in 1940 developed a method called orthoganalized plane wave (OPW). This method gives reasonably good results for simple metals. In complicated cases, one has to supplement variational technique for the expectation value of the energy with the OPW functions. It has been shown by Parmenter[14] that the tight binding method discussed earlier goes over to the OPW method when the tightly bound electron becomes free.

The other way of improving the method of band structure calculation is to look at the potential function of the lattice itself. Selecting a constant potential in the inter-ionic region and a spherical atomic potential surrounding each ion a method known as augmented plane wave (APW) was developed by Slater[17] in 1937. In this method the wave function consists of two parts, namely, a solution within the atomic sphere expanded in spherical harmonics and a plane wave in the inter-ionic region. This method in conjunction with the recent mathematical technique[18,19,20] has been proved to be a powerful technique of band structure calculation.

There is another method, which makes use of Wannier functions[21] (Koster,[22] Parzen,[23] and Wain Wright & Parzen[24]). This method is not so easy to handle as the mathematics involved is difficult.

However, from the above methods it is found that the calculated electronic energy levels ~~is~~ are not in good agreement with the experimental results. Thus to get a closer agreement between the calculated energy levels and the experimental results one has to do a self-consistent field calculation.

In the foregoing discussion of the band structure we have considered the nature of the stationary electronic states. It is interesting to consider the influence of external fields on these stationary electronic states. In the periodic field of the crystal, the charge carrier moves with a group velocity

$$\underline{V}_{\underline{k}} = \frac{1}{\hbar}\left(\frac{\partial E_{\underline{k}}}{\partial \underline{k}}\right) \tag{1.9}$$

and its motion in the applied external field is described by the time-dependent Schrödinger's equation.

$$(H_o + H')\ \psi(\underline{r}, t) = i\hbar\ \frac{\partial\psi}{\partial t}(\underline{r}, t) \tag{1.10}$$

where $(\underline{r}, t)$ is the electronic wave function. H_o is the Hamiltonian in the absence of the external field and H' is the Hamiltonian for the external field of force. Writing

$$H_o = \frac{-\hbar^2\nabla^2}{2m^*}$$

one can get the effective mass equation of the electron as

$$\left(\frac{-\hbar^2\ \nabla^2}{2m^*} + H'\right)\ \psi(\underline{r}, t) = i\hbar\ \frac{\partial\psi(\underline{r}, t)}{\partial t} \tag{1.11}$$

originally due to Wannier.[21] Here $1/m^*$ is given by the expression (1.6).

C. PHONONS

In the foregoing section, we have discussed the dynamics of the charge carriers in a crystal lattice. Now we shall consider the state of the crystal lattice at any finite temperature. The ions of the lattice execute small oscillations about their equilibrium position. These ions are coupled to one another by elastic forces and the small displacements from the equilibrium position acts as a disturbance in the crystal lattice. One can describe these lattice displacements in terms of a wave pattern travelling in the crystal lattice, called lattice waves. Each such wave is characterised by a wave vector $\underline{q}$ and a frequency $w_{\underline{q}p}$. Here p is the mode branch number of the lattice wave. Alternatively, the lattice vibrations can be represented as a vibrational field in which the field variables are the displacements of the ions from their equilibrium positions. In the language of quantum field theory this can also be described as a cloud of quanta~~s~~ of the vibrational field, known as "Phonons". The Hamiltonian for the lattice vibrational system can be written as[5]

$$H_L = \frac{1}{2} \sum_{\underline{l},\underline{b}} \left[\left(\frac{1}{M_{\underline{b}}}\right) \underline{p}^{*}_{\underline{l},\underline{b}} \; p_{\underline{l},\underline{b}} + V(R_{\underline{l},\underline{b}}) \right] \qquad (1.12)$$

where $\underline{l}$ is the vector of the origin of the cell to which the atom belongs, $\underline{b}$ is the basis vector to the atom in the cell.

$R_{\underline{l},b}$ is the displaced position of the $(\underline{l},\ \underline{b})^{th}$ atom from the equilibrium position. The displacement

$$\delta R_{\underline{l},\underline{b}} = R_{\underline{l}\ \underline{b}} - (\ \underline{l} + \underline{b})$$

M_b is the mass of the ion in motion, $p_{\underline{l}\underline{b}}$ is the momentum operator. The potential energy $V(R_{\underline{l}\ \underline{b}})$ can be expanded in Taylor's series in terms of the various displacements as

$$V(\underline{R}_{\underline{l},\underline{b}}) = V_o + \tfrac{1}{2} \sum_{\underline{l},\underline{b}} \sum_{\underline{l}'\ \underline{b}'} \delta \underline{R}_{\underline{l},\underline{b}} \left(\frac{\partial^2 V}{\partial R_{\underline{l}\ \underline{b}}\, \partial R_{l'b'}} \right) \delta \underline{R}_{\underline{l}'\underline{b}'} + \cdots$$

$$= V_o + \tfrac{1}{2} \sum_{\underline{l}\ \underline{b}} \sum_{\underline{l}'\underline{b}'} \delta \underline{R}_{\underline{l},\underline{b}} \cdot G_{\underline{l},\underline{b};\underline{l}'\underline{b}'}\, \delta \underline{R}_{\underline{l}'\underline{b}'} + \cdots \qquad \ldots\ldots\ldots (1.13)$$

where we have retained terms only upto second order in the Taylor's expansion. This is known as the Harmonic approximation. Now the expression (1.12) can be written within the frame work of harmonic approximation,

$$H_L = \tfrac{1}{2} \sum_{\underline{l},\underline{b}} \left(\frac{1}{M_{\underline{b}}}\right) p^{*}_{\underline{l}\underline{b}} \cdot p_{\underline{l}\underline{b}} + \tfrac{1}{2} \sum_{\underline{l},\underline{b}} \sum_{\underline{l}'\underline{b}'} \delta R_{\underline{l}\underline{b}} \cdot G_{\underline{l}\underline{b};\underline{l}'\underline{b}'} \cdot \delta R_{\underline{l}'\underline{b}'} \qquad \ldots\ldots\ldots (1.14)$$

It is convenient to represent the operators $p_{\underline{l}\underline{b}}$ and $\delta R_{\underline{l}\underline{b}}$ in terms of the new operators $b^{*}_{\underline{q}\underline{p}}$, $b_{\underline{q}\underline{p}}$ as

$$\delta R_{\underline{l}\underline{b}} = -i\left(\frac{\hbar}{2NM_{\underline{b}}}\right)^{\frac{1}{2}} \sum_{\underline{q},\underline{p}} e_{\underline{q},\underline{b},p}\; w_{\underline{q}p}^{-\frac{1}{2}} \left(b^{*}_{\underline{q},p} - b_{\underline{q},p}\right) e^{-i\underline{q}\cdot\underline{l}}$$

$$P_{\underline{l}\underline{b}} = \left(\frac{\hbar M_{\underline{b}}}{2N}\right)^{\frac{1}{2}} \sum_{\underline{q},p} e_{\underline{q},\underline{b},p}\; w_{\underline{q}p}^{\frac{1}{2}} \left(b_{\underline{q},p} + b^{*}_{-\underline{q}p}\right) e^{i\underline{q}\cdot\underline{l}}$$

...... (1.15)

Here $e_{\underline{q},\underline{b},p}$ denotes the polarization vector. With the help of (1.15) the Hamiltonian (1.14) becomes

$$H_L = \sum_{\underline{q},p} \left(b^{*}_{\underline{q}p}\, b_{\underline{q}p} + \frac{1}{2} \right) \hbar\, w_{\underline{q},p} \qquad (1.16)$$

The expression (1.16) represents the Hamiltonian for the harmonic oscillator with $N_{\underline{q}p} = b^{*}_{\underline{q}p}\, b_{\underline{q}p}$ as the occupation number operator with positive integers as eigen values. It is evident from the expression (1.16) that the vibrational field of the lattice vibration can be regarded as a system of non interacting Boson particles called phonons, each having an energy $\hbar w_{\underline{q}p}$. The operators $b^{*}_{\underline{q}p}$, $b_{\underline{q}p}$ are known as phonon creation and annihilation operators, respectively and they satisfy the commutation relations

$$\left[b_{\underline{q}p},\, b^{*}_{\underline{q}'p'} \right] = \delta_{\underline{q}\,\underline{q}'} \cdot \delta_{p\,p'} \qquad (1.17)$$

In the above treatment, we have considered a three - dimensional lattice with more than one atom per unit cell. This model leads to polarization and dispersion in the frequency spectrum of the lattice vibration. For a cubic crystal with the wave vector $\underline{q}$ of the lattice wave along a symmetry axis, the polarization direction may be fixed by symmetry arguments. This will lead to the notion of the longitudional and transverse modes of vibration. For arbitrary $\underline{q}$, this type of classification of the vibrational mode is approximately valid. The longitudinal mode is essentially a compressional wave and the transverse mode is a shear wave. The presence of more than one atom in the unit cell leads to two different modes of vibration known as the acoustic and the optical modes. In the acoustic mode the atoms of the unit cell move in the same direction and in the optical mode they move in the opposite direction. The frequency of the acoustic mode tends to zero as the wave vector q_a of the acoustic phonon tends to zero. In the Debye model the acoustic mode frequency is proportional to $\underline{q}_a$ and can be put in the form $w_{\underline{q}_a} = c\underline{q}_a$ where c is the velocity of the sound wave in the elastic continuum. Thus, the acoustic vibrations in the long-wave length can be treated as elastic waves of a continuum. For the optical modes the frequency lies in the infra-red region of the electromagnetic radiation.

Further, when the atoms of the unit cell are charged, the counter motion of the atoms, causes a polarization in the lattice and the optical modes are then called as polar modes.[25] These polar optical modes play an important role in polar semiconductors.

D. SCATTERING MECHANISMS:

In order to understand the various electrical, thermal and magnetic effects, it is essential to think of the role of several types of imperfections that occur in a real crystal. In a perfectly crystalline solid the charge carriers move without any resistance. The imperfections of the crystal restrict the motion of the charge carriers. The imperfections may owe their origin to thermal effects (phonons), to impurity atoms, or to the lattice disorder owing to the presence of the foreign atoms to form solid solution (alloying effect) and other deviations from the perfect periodicity.

In this section we consider the role of the first three types of lattice imperfections on the motion of the charge carriers. Now the dynamical system under consideration is the electron and phonon systems in thermal equilibrium. These are distributed according to their distribution functions, $n^{o}_{\underline{k}}$, $\overline{N}_{\underline{q}p}$ respectively. Under the influence of an external field the equilibrium distribution function of the charge carriers will change and they relax back to their equilibrium value by a collision process and this process is described by the well known Boltzmann transport equation for the charge carriers in the steady state[6]

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{Coll} = \frac{\underline{F}}{h} \cdot \mathrm{grad}_{\underline{k}}\, n_{\underline{k}} + \underline{V}_{\underline{k}} \cdot \mathrm{grad}_{\underline{r}}\, n_{\underline{k}} \qquad (1.18)$$

where $n_{\underline{k}}$ is the new distribution function of the electrons

$\underline{V}_{\underline{k}}$ being their velocity, $\underline{F}$ is the external field. In the discussion of a collision mechanism it is usual to assume that the rate of relaxation is proportional to the deviation of the distribution function from the equilibrium value and to define a relaxation time τ by means of the equation

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{Coll}} = - \frac{n_{\underline{k}} - n_{\underline{k}}^{o}}{\tau} \qquad (1.19)$$

In the above discussion, it is assumed that the phonon distribution will remain same at their equilibrium value. The relaxation time τ is related to the probability of scattering per unit time from a state $\underline{k}$ to $\underline{k}'$ as shown below. Following Nordheim,[26] one can relate the transition probability and $\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{coll}}$, by means of the equation

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{coll}} = \int \left[P(\underline{k}',\underline{k})n(\underline{k}')(1-n(\underline{k}) - P(\underline{k},\underline{k}')n(\underline{k})(1-n(k')) \right] d\underline{k}' \qquad \ldots\ldots (1.20)$$

where the transition probabilities

$$P(\underline{k}',\underline{k}) = \underline{P}(\underline{k},\underline{k}') = \frac{2\pi}{\hbar} \left| \langle \underline{k}' | H' | \underline{k} \rangle \right|^2 \delta(E_{\underline{k}}-E_{\underline{k}'}), \qquad \ldots\ldots (1.21)$$

and $\delta(E_{\underline{k}} - E_{\underline{k}'})$ is the δ- function ensuring energy conservation and $\langle \underline{k}' | H' | \underline{k} \rangle$ is the matrix element of the interaction Hamiltonian which represents the interaction energy between the electron and the scattering system. Further it is convenient to introduce a quantity μ called the charge carrier mobility by means of the equation

$$\mu = \frac{e\tau}{m^*} \text{ (cm}^2\text{ / Volt - sec)}, \qquad (1.22)$$

where e is the charge and m^* is the effective mass of the charge carrier. Alternatively, μ is the magnitude of the average drift velocity of electrons in unit electric field and by convention it is a positive quantity.

The relaxation time is in general a function of $\underline{k}$ and explicitly depends on the type of the scattering mechanisms that arise in the crystal lattice. Hence, the scattering mechanism plays an important role in the mobility problem.

(1) Lattice Scattering:

The thermal motion of the ions about their equilibrium position introduces an additional potential δV in the lattice. This additional potential may be considered as a small perturbation and an electron in the state $\underline{k}$ can undergo transition to a state $\underline{k}'$ by emission or absorption of a phonon. By expanding the actual potential about the equilibrium value in Taylor's series and retaining only the linear term we can represent additional potential as[5]

$$\delta \underline{V} = \sum_{l,b} \left(\frac{\partial V}{\partial \underline{R}_{l,\underline{b}}} \right) \cdot \delta \underline{R}_{l,\underline{b}}$$

Here δV is a linear function of the displacement vector $\delta \underline{R}_{\underline{l},\underline{b}}$. This additional potential represents the total change in the Hamiltonian of the unperturbed system, when the lattice ions are displaced. The matrix element of the scattering process can be written as

$$M(\underline{k},\underline{k}') = \sum_{l,b} \int \bar{\psi}_{\underline{k}} \frac{\partial V}{\partial \underline{R}_{lb}} \psi_{\underline{k}'} \, d\underline{r} \cdot \left\langle N_{\underline{q}p} \middle| \delta \underline{R}_{lb} \middle| N_{\underline{q}p}{}^{-1} \right\rangle$$

Here ψ_{k}'s are electron state functions and $|N_{\underline{q}p}\rangle$'s are phonon state functions in the occupation number representation.

In order to write down the specific form of the matrix element, we consider a simplified model of a semiconductor namely, a non-degenerate semiconductor with constant spherical energy surface and band extrema at $\underline{k} = 0$ (standard band model). For this model one can safely assume the lattice scattering to be elastic. It can be shown that with the aid of the conservation laws of energy and momentum that an electron interacts with the longitudional acoustic modes and the maximum value of the acoustic phonon wave vector that is effective in the scattering process is equal to $q_{max} \leq 2k$. Further, the wave vectors of the electrons of interest are small compared to the dimensions of the Brilloium zone for semiconductors with the above mentioned characteristics. Here it may be pointed out that the transverse modes are unimportant and may be neglected.[27] But in general transverse modes do indeed contribute to the relaxation process. When the band structure has the many-valley model found in n-type Ge and Si, Bardeen and Shockley[28] have developed a very convenient and powerful method of calculating the lattice scattering in non-polar semiconductors. The method is based on the concept of a deformation potential and the effect of the dilation on the band edges, centred at $\underline{k} = 0$, can be expressed as

$$E_c - E_{c_o} = \varepsilon_d \, \Delta r \quad , \qquad (1.23)$$

where E_c and E_{c_o} are the conduction band edge energies after and before dilation respectively, Δr is the dilation and ε_d is the deformation potential. The matrix element for the electron-phonon scattering is given by[5]

$$M(\underline{k},\underline{k}') = \langle \underline{k}' \,|\, H' \,|\, \underline{k} \rangle = \left(\frac{\hbar N_{\underline{q}_a}}{2MNVw_{\underline{q}_a}} \right)^{\frac{1}{2}} q_a \, \varepsilon_d \qquad ..(1.24)$$

where q_a is the wave vector of the acoustic phonon. Using the form (1.24) for the matrix element in (1.19) and (1.20), it can be shown that the relaxation time

$$\tau = \frac{c^2 \hbar^4}{8\pi^3 \, (2m^*)^{3/2} \, (k_B T) \, \varepsilon_d^2 \, E^{\frac{1}{2}}} \qquad ..(1.25)$$

and the lattice mobility obeys a $T^{-3/2}$ law.

The acoustical modes also give rise to a polar type of lattice scattering called piezoelectric scattering in a crystal having charged atoms in the unit cell and lacking a centre of symmetry. This type of scattering will not arise as the system to be considered in the present thesis possesses a centre of symmetry.

Let us now consider the role of optical modes of lattice vibration in the relaxation processes. From the dispersion relation for the optical mode it is evident that the frequency of the optical modes is high compared to that of the acoustic mode. The longitudinal optical mode satisfy the relation $\hbar w_1 = k_B \theta$, where θ is called the characteristic temperature and k_B is the Boltzmann constant and w_1 is the frequency of the longitudinal optical mode. From the laws of the conservation of energy and momentum it follows that the optical modes are able to interact with an electron having a wave vector modulus k_θ. At temperatures $T \leqslant \theta$ optical modes having wave vector within the range $0.4\, k_\theta < q_o < 2.4\, k_\theta$ can contribute to scattering. In the case of the non-polar optical modes (pure optical modes), the method of deformation potential was introduced by Seitz[31] in 1948. Following his discussion, we can write the matrix element of the optical mode scattering as

$$M(k,k') = i \left(\frac{\hbar N_{q_o}}{2\, MNVw_{q_o}} \right)^{\frac{1}{2}} g\, \mathcal{E}_3 \qquad (1.27)$$

where $\mathcal{E}_3$ is the deformation potential for optical modes and w_{q_o} is the optical mode frequency. At high temperature $(T > \theta)$ the optical mode scattering gives rise to the same mobility temperature relation namely $\mu \propto T^{-3/2}$ except for a numerical factor. But at low temperatures there is one essential difference arising from the dominating factor $(e^{\theta/T}-1)$.

When the atoms of the unit cell are charged, then the optical modes of lattice vibration will introduce polarization waves into the lattice. Following the theory given by Frohlich[32] the matrix element of the polar mode scattering can be written as

$$M(k,k') = 4\pi i \left(\frac{e^2 h}{2 \gamma w_{\underline{q}_0} V} \right) \frac{N^{\frac{1}{2}}_{\underline{q}_0}}{q_0} \qquad (1.28)$$

where

$$\frac{1}{\gamma} = \frac{w^2_{\underline{q}_0}}{4\pi} \quad \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \qquad (1.29)$$

Here ϵ_∞ and ϵ_0 are the high frequency and static dielectric constants repsectively. $w_{\underline{q}_0}$ is the polar mode frequency. In the high temperature region i.e. $T > \theta$, the mobility is proportional to $T^{-\frac{1}{2}}$. At low temperature, however, it is proportional to $(e^{\theta/T} - 1)$ as obtained by Frohlich. In Frohlich's formulation a weak coupling between electron and optical phonon was assumed (coupling constant; $\alpha < 1$). Howrath and Sondheimer[30] in 1953 calculated in the weak coupling limit a mobility expression for the whole temperature region in a non-degenerate semiconductor and found that in the low temperature region, their formula reduces to Frohlich's[32] expression. In the intermediate coupling region ($1 < \alpha \leqslant 3$) Low and Pines[33,34] developed a theory for the polar mode scattering process and the formation of

Polaron[*] becomes noticeable in this region. As we are interested in the weak-coupling region, the polaron formation need not be considered in the present investigation.

(2) Impurity Scattering:

Static imperfections such as impurity atoms that may be present in a crystal lattice are also effective in scattering the charge carriers. The impurity atoms may be charged or neutral. Obviously charged impurity atoms play an important role in scattering the charge carriers and comparatively the role of the neutral impurities is less significant.

Let us consider first the ionized impurities distributed randomly over the lattice sites. The coulomb field of the impurity atoms scatters the electron and the scattering can be shown to be elastic and anisotropic and scattering at small angles predominates. It is found that unless one takes the modified coulomb potential for the impurity atoms, divergence in the scattering cross section will occur. Also it is reasonable to consider some modifications of the coulomb potential for the impurity atoms, as the atoms are present in the crystal lattice. Conwell and Weisskopf[35] have given a method for calculating the scattering process and obtained an

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[*] An electron in an ionic lattice induces ionic polarization and moves with the polarization waves. This single entity of an electron and its associated waves of ionic polarization is called a polaron.

expression for the impurity mobility, $\mu_I \propto T^{3/2}$. In deducing the mobility expression they have assumed that the coulomb field ceases to be effective at a radius R_m equal to half the mean distance between impurity atoms. Brooks,[36] Herring[37] and Dingle[38] have presented another approach to the study of the scattering process by considering the screening of the coulomb field due to the redistribution of the charge carriers. The form of the coulomb potential is

$$V(\underline{r}) = -\frac{Ze^2}{r}\exp\left(-\frac{r}{R_m}\right) \tag{1.30}$$

As before a random distribution of the impurity atoms was considered. Again a $T^{3/2}$ law for the expression was noticed with the difference in the logarithmic term in the mobility expression.

The above methods are based on the Born approximation, hence it is valid only in the temperature region which are sufficiently high. Further, the above theory is restricted to a standard band model. Modifications in the mobility expression will arise if one takes note of the deviation from the spherical energy surface. The exact calculation of the relaxation time is difficult. However, deviations from $T^{3/2}$ law for the impurity mobility have been noticed. On numerical integration it was found by Blatt[27] that the mobility expression of Brooks[36] and Herring represents the experimental situation provided the contribution of the logarithmic term towards the temperature dependence was taken into account.

Neutral impurity atoms can be considered as hydrogen atoms in a dielectric medium. The scattering cross section has been given by Erginsoy[39] and he found that the relaxation time is isotropic for spherical energy surfaces. The relaxation time is independent of the electron energy and the temperature.

(3) Alloy Scattering:

In the foregoing section, we have considered the role a single point imperfection in the scattering of the charge carriers. When the impurity concentration is high the methods adopted in the previous section seem to be unrealistic and one has to consider the role of the alloys in the scattering processes. We consider only substitutional alloys for simplicity as done by Nordheim[26] and Muto.[40] According to them the electrons move in an average potential substituted for the actual potential at the lattice site and the ~~average~~ difference potential is treated as a perturbing potential. They found that the square of the matrix element of the perturbing potential is proportional to $f_s(1-f_s)$, where f_s is the concentration of the s type atom in the alloy.

CHAPTER - 2

A. POLAR SEMICONDUCTORS:

In semiconducting crystals two types of forces are important. They are (1) the classical concept of coulomb force between the charges illustrated by the polar bond in ionic crystals and (2) the quantum mechanical concept of the sharing of electrons leading to a covalent bond. In general both type of forces exist in a semiconducting crystal. If the polar bond is dominant, the semiconductor is called a polar semiconductor and if the covalent bond is dominant, it is called a valence semiconductor. The element semiconductors of the IV group of the periodic table namely, Germanium and Silicon, are the well known examples of valence semiconductors. The lead compounds PbS, PbSe and PbTe are the typical examples of the polar semiconductors.

The lead chalcogenides noted above are polar semiconductors and their physical properties have been reviewed by Scanlon.[41] The important points to note are the following:

1) They do not form exact stoichiometric compounds owing to the polar character of the material and any deviations from stoichiometric produces an n-type or a p-type semiconductor,

2) The energy gap is small and is of the order 0.3 ev,

3) The ratio of the effective masses of the charge carrier to the free electron mass vary from 0.1 to 0.5,

4) They are classed as II - VI group semiconductors and crystallize~~s~~ in the sodium chloride structure (interpenetrating f. c. c.)

5) The mobility of the charge carriers is high and seems to be independent of their nature and concentration. The temperature dependence is of the type $\mu = \mu_0 T^{-n}$ where n = 2.5. The $T^{-5/2}$ behaviour is observed over a wide temperature range from about 500°K to 80°K.

From the experimental facts noted above it is evident that the behaviour of the electrons in polar semiconductors is much more complicated than the conventional covalent semiconductors. However, for the system under consideration, it is possible to undertake a theoretical investigation of the electronic processes.

At this stage, it is essential to distinguish between the system under consideration and another class of polar semiconductors (e.g. NiO) for which the band picture is not valid. In such semiconductors it is found that the electron mobility is very low (~ 1 cm^2 / volt-sec.) and the electrons do not experience any periodicity of the polar lattice and one has to take recourse to the localized wave functions of the carriers. However, in PbS system the band picture remains valid and one would expect a stronger interaction of the charge carriers with the polar lattice.

We have seen in the previous section that in the high temperature region ($T > \Theta$) the acoustic mode scattering of the electron gives the law $T^{-3/2}$, and the theory based on the optical polar mode scattering shows the dependence as $T^{-1/2}$, for the mobility. On the other hand Fröhlich-Mott[42] theory of scattering with the polar modes of vibrations suggests the temperature dependence $\mu \propto (e^{\theta/T}-1)$. Evidently, it is not possible to explain the mobility behaviour in terms of the scattering of the charge carriers independently with the acoustical or the optical modes above the characteristic temperature.

In order to explain the typical mobility behaviour observed in the PbS family of semiconductors attempts have been made by Hirahara and Murkami,[43] Petritz and Scanlon[44] by combining the reciprocal mobilities of the various independent processes namely, the acoustic mode scattering, the optical mode scattering and the ionized impurity scattering, etc. The expression for the reciprocal mobility is given by

$$\frac{1}{\mu} = A\,T^{+3/2} + B\,T^{-3/2} + C\,(e^{\theta/T}-1)^{-1} \tag{2.1}$$

Here the first term is the contribution from the acoustic mode scattering, the second term is due to the ionized impurity scattering and the third term is due to the polar modes of lattice vibrations. Hirahara and Murakami[43] have neglected the reciprocal mobility compared with the contribution from the ionized impurity scattering and determined the constants A, B and C that occur in the expression (2.1) by fitting the equation to the observed mobility value. Similar methods have been adopted by Petritz and Scanlon[44] to analyse the mobility data. They have assumed that the contribution from the ionized impurity scattering process is unimportant in the temperature range of interest. Hence the mobility expression is given by

$$\frac{1}{\mu} = A\,T^{+3/2} + \frac{C\,(\theta/T)^{\frac{1}{2}}}{(e^{\theta/T} - 1)\,\chi_{(\theta/T)}} \qquad (2.2)$$

Here, as before, the first term arises from the acoustic mode scattering and the second term is due to polar mode scattering (Frohlich-Mott[42] and Howarth-Sondheimer[30]). It is found that for $\theta \sim 200$°K in the high temperature region ($T > \theta$), the mobility expression (2.2) does not represent the experimental situation. However, in the low temperature range ($T < \theta$), the agreement was fair but the experimental values are much lower than those predicted by the theory. It is evident from the above theories that by combining the reciprocal mobilities of the various scattering processes, the experimental facts can not be explained satisfactorily.

The polar scattering theory alone does not seem to explain the mobility behaviour as the function ($e^{\theta/T} - 1$) is concave upward when plotted on a log-log scale, whereas the experimental curve is concave downward.

Tolpygo and Fedorchenko[45] analysed the mobility problem in a diamond type non-polar semiconductor$ invoking an additional deformation force induced by a hole and obtained a $T^{-5/2}$ law for the mobility expression at high temperature. Such an analysis is perhaps not appropriate for the polar semiconductors under consideration.

B. SOLID SOLUTIONS OF THE LEAD CHALCOGENIDE SYSTEM

In the previous section, we have considered the charge carrier mobility behaviour of the pure polar semiconductors and we found that it is proportional to $T^{-5/2}$. We also saw that the earlier theories were unable to resolve the difficulties encountered. Now, we shall consider, in what follows, the behaviour of the charge carriers in the solid solutions of the lead chalcogenide system.

The three compounds PbS, PbSe and PbTe are isomorphous and they have a common cation. One may expect solid solutions of these compounds to exist in all proportions.[46] Experimentally, it has been established that only PbS+PbSe and PbSe+PbTe alloys can be prepared in all proportions.

It is interesting to consider the mobility behaviour in the solid solutions of isomorphous compounds. This has been studied in great detail by Kolomoets et al.[47] (The main idea of such a study was to increase the ratio μ/K_{ph} where K_{ph} is the lattice thermal conductivity[48]). They have shown that the mobility of the electrons or holes depends on the concentration of one of the components of the alloys and on temperature. Hence alloying effects do indeed play an important role in the mobility problem. In the solid solutions of PbSe+PbTe, the mobility in the high temperature region is proportional to $T^{-5/2}$, whereas in the low temperature region it varies as $T^{-3/2}$ ($T > 50°K$).[48]

Nordheim[26] calculated the alloy contribution to the residual resistance, considering the scattering of the charge carriers by the random distribution of the alloy atoms over the lattice sites. He found that the relaxation time can be expressed as

$$\frac{1}{\tau} = C_1 f_s (1 - f_s) E^{\frac{1}{2}} \qquad (2.3)$$

where, E is the energy of the conduction electrons, C_1 is a temperature independent factor which includes the strength of the scattering and the effective masses of the electrons. For thermal scattering we have seen earlier that the relaxation time is given by,

$$\frac{1}{\tau} = C_2 E^{\frac{1}{2}} \qquad (2.4)$$

C_2 is a parameter which determines the scattering strength and effective mass of the electron. Herman, Glickman and Parmenter[49] have considered in their review article, the addition of reciprocal mobilities of the independent processes, namely, thermal and alloy scattering, to obtain a resultant mobility.

Brooks[50] obtained a $T^{-1/2}$ law for the mobility expression in the Ge - Si alloy system. The treatment consists in representing the alloy potential function in terms of the band energies of the pure elements arranged at random. The parameters in the mobility expression were calculated using experimental data on Ge and Si. The equality of the thermal mobility and disorder mobility for 8 % Si in Ge was predicted. This prediction has been confirmed by Glicksman[49] for 9 % Si in Ge.

C. APPROACH TO THE MOBILITY PROBLEM:

It is clear from the discussions of the previous section, that the earlier theories[43,44] of the mobility of charge carriers in polar semiconductors are inadequate. The entire situation demands a radically new line of thinking. In our present study we invoke certain new concepts and obtain a consistent theory of carrier mobility in polar semiconductors (PbS group) and their solid solutions.

Let us consider the mobility behaviour in the pure cases, namely, PbS, PbTe and PbSe. A knowledge of the band structure of a semiconductor is of great importance in the understanding of the transport properties of the substance. There are a number of theoretical calculations[13,51] and experimental measurements[52,53,54] relating to the band structure of lead chalcogenides. These show that the band structure differs from the conventional covalent semiconductors in the sense that the conduction and valence bands in the lead chalcogenides may be similar. According to Bell et al.,[13] in PbS the full s and p bands derive from the 6s and 3p levels of Pb and S respectiverly and the first empty band arises from the 6p levels of Pb. This empty band has the same symmetry as the full valency p band and furthermore, it overlaps with a band which has the same symmetry as the full s band. The differences in energy between direct and indirect transition are not appreciable and they are within the range $k_B\theta$ (Scanlon;[46] Smirnov, Moizhes and Nernsberg[55]).

Thus from the band structure noted above, it is apparent that they will interact strongly with one another and with lattice vibrations (both acoustical and optical or polar modes).

The interaction of the carriers with the lattice vibration would seem to be of particular importance in the interband mixing. In this context it is hard to imagine that the carriers belong strictly to one pure band. Phonon assisted inter-band mixing is more likely and will have an important role in the transport properties. There is indeed an experimental observation showing the thermal excitation of carriers into higher bands.[56]

In the first part,[57] we consider the role of optical modes (or polar modes) in the inter-band transition and for the scattering both the roles of acoustic and optical modes are taken into account. This mechanism is assumed in the formal development of the theory. The relevant relaxation time and the mobility expressions are derived assuming the spherical ~~and~~

~~parabolic~~ band for the PbS group. This seems to be supported by the recent work on PbS and PbSe (Bir and Pikus,[58] Palik et al.[59]).

In the second part,[60] we extend the theory to the case of solid solutions of PbS group. The extension resides in taking into account additional perturbations owing to the alloying effect. It is assumed that such perturbations are also capable of causing inter-band mixing of the carriers in the solid solutions. From a simple crystal field model (see appendix) it will be shown that the alloying effect does indeed give rise to inter-band transitions. We shall then develop a theory of transport of carriers in these solid solutions whose orbital functions are modified owing to the change in the crystal potential as a result of alloying. The relevant relaxation time and the mobility expressions are derived under the same assumptions as done in the first case.

CHAPTER - 3

A. FORMULATION OF THE INTERACTION HAMILTONIAN

(1) PbS Group.[57]

We consider a system of the type MX crystallizing in cubic rock salt structure, where M is the metal ion and X is the anion. In the present system under investigation M = Pb, X = S, Se or Te. There will be one or more valence electrons for each type of atom in addition to the closed shell of electrons. These valence electrons are supposed to move in the average periodic potential of the ion cores and the other electrons. Hence it is essentially a one electron problem. The Hamiltonian of the system is

$$H = H_e + H_L + H_{int} \tag{3.1}$$

Here H_e is the electronic part of the one electron Hamiltonian and can be written as

$$H_e = \frac{-\hbar^2 \nabla^2}{2m} + V(\underline{r}) \tag{3.2}$$

where $\frac{-\hbar^2 \nabla^2}{2m}$ is the kinetic energy operator, and

$$V(\underline{r}) = \sum_m V_m (\underline{r} - \underline{R}_m^o) + \sum_l V_l (\underline{r} - \underline{R}_l^o) \tag{3.3}$$

is the periodic potential experienced by an electron at $\underline{r}$ comprising the potential due to the ion cores of the metal ions and anions while in their equilibrium positions $\underline{R}_m^o$ and $\underline{R}_l^o$ respectively. H_L is the lattice Hamiltonian expressed as in equation (1.16).

$$H_L = \sum_{q} \frac{\hbar w_{\underline{q}}}{2} (b_{\underline{q}} b^*_{\underline{q}} + b^*_{\underline{q}} b_{\underline{q}})$$

$$= \sum_{q} \hbar w_{\underline{q}} (b^*_{\underline{q}} b_{\underline{q}} + \frac{1}{2}) \qquad (3.4)$$

Here we have omitted the mode branch number p as we consider only longitudanal modes in the calculations. H_{int} is the interaction Hamiltonian which arises due to the vibration of the atoms around their equilibrium positions. In effect, this constitutes the electron-lattice interaction terms. The fact that the system under consideration contains two types of atoms per unit cell, namely, one of M type and another X type, helps us to separate the H_{int} into two parts i.e.

$$H_{int} = P + A \qquad (3.5)$$

Here, P is the perturbation owing to the optical (or polar) modes of lattice vibrations and A refers to the perturbation arising from the acoustical mode. In order to get the explicit form of P and A in (3.5) a specific model should be considered. In the present theory we consider two models, namely (1) Atomistic model and (2) Continuum model.

Let us consider the form of P and A in the atomistic model. In this model, we take into account the oscillations of the nearest neighbour ions into account. For small displacements, we can expand the potential energy function around the equilibrium positions of atoms in Taylor's series as done in equation (1.13). Then the interaction term can be written as

$$H_{int} = \sum_{n,h=nn} \left(\frac{\partial V}{\partial \underline{R}_{\underline{h}}}\right)_{o} \cdot \delta R_{\underline{h}} + \sum_{n,h,h'} \delta \underline{R}'_h \cdot \left(\frac{\partial^2 V}{\partial \underline{R}'_h \partial \underline{R}_h}\right)_{o} \cdot \delta \underline{R}_h + \cdots \qquad \ldots\ldots.(3.6)$$

Here, $\delta \underline{R}_h$ is the relative displacement vector and is given by $\delta \underline{R}_h = \delta \underline{R}_n - \delta \underline{R}_m$ where n, m are the nearest neighbour atoms. We denote this by writing $h = nn$ (i.e. nearest neighbours). We restrict our attention to the first term in (3.6). Further, it is expedient to express the relative displacement $\delta \underline{R}_h$ in terms of the phonon creation and annihilation operators as given by (1.15).

Then

$$H_{int} = \sum_{n,h=nn} \left(\frac{\partial V}{\partial \underline{R}_n} \right)_o \cdot \delta R_h$$

$$= \sum_{n,h=nn} g_{\underline{q}} \left(\frac{\partial V}{\partial \underline{R}_h}\right)_o \cdot e_{\underline{q}n} \left[\exp(iq.\underline{R}_n) \pm \exp(iq.\underline{R}_m) \right] (b^*_{\underline{q}} - b_{-\underline{q}}) \qquad \ldots\ldots.(3.7)$$

where

$$g_q = \frac{1}{\sqrt{N}} \left(\frac{\hbar}{2M\, w_q} \right)$$

and $e_{\underline{q}n}$ is the unit polarization vector associated with atom n. In (3.7) the plus sign refers to the optical mode and minus to the acoustical mode. M is the mass of the atoms M and X assumed to be equal.

We make use of the approximation, namely,

$$\left(\frac{\partial V}{\partial \underline{R}_n}\right)_o \cdot \delta R_n = \left|\frac{\partial V}{\partial \underline{R}_n}\right| \; \left|\delta \underline{R}_n\right|$$

i.e. they are parallel.

Hence the decomposition of (3.7) and (3.5) is obvious. We will have

$$P = \sum_{n} \sum_{\underline{q}_o} \sum_{h=nn} g_{\underline{q}_o} F(\underline{r}, R_n)(e^{i\, \underline{q}o \cdot \underline{R}n} + e^{i\, qo \cdot \underline{R}m}) \times (b^{*}_{q_o} - b_{-\underline{q}_o}) \qquad \ldots(3.8)$$

$$A = \sum_{n} \sum_{q_a} \sum_{h=nn} g_{\underline{q}_a} F(\underline{r}, \underline{R}_n) (e^{i\, q_o \cdot R_n} - e^{i\, q_o \cdot R_m}) (b^{*}_{\underline{q}_a} - b_{-\underline{q}_a}) \qquad \ldots(3.9)$$

Where

$$F(\underline{r}, \underline{R}_n) = \pm |Qe^2| \left(\frac{1}{R_n^2} + \frac{2z}{2R_n^3} + \frac{3}{2} + \frac{3z^2 - r^2}{R_n^4} + \ldots \right) \qquad (3.10)$$

and z, $\underline{r}$ stand for the electronic co-ordinates and $\underline{R}_n$ denotes the distance between the nearest neighbours. The plus and minus signs refer to the two situations i.e. whether the carrier interacts with the positive or negative ion. The subscripts "o" and "a" in (3.8) and (3.9) stand for the optical and acoustical modes respectively.

In the continuum model one can again write down the explicit forms of P and A which may be more convenient for calculations. Thus, we formally write P and A in (3.5) as

$$P = \sum_{\underline{q}_o} P_{\underline{q}_o} \left(b^*_{q_o} e^{-i\, \underline{q}_o \underline{r}} - b_{q_o} e^{i\, \underline{q}_o \cdot \underline{r}} \right) \qquad (3.11)$$

$$A = \sum_{\underline{q}_a} A_{\underline{q}_a} \left(b^*_{\underline{q}_a} e^{-i\, \underline{q}_a \underline{r}} - b_{q_a} e^{-i\, \underline{q}_a \cdot \underline{r}} \right) \qquad (3.12)$$

where the coefficients $P_{\underline{q}_o}$ and $A_{\underline{q}_a}$ may be functions of both the phonon propagation vectors as well as the electron coordinates at site n. In the Frohlich's formulation of the polar modes[5]

$$P_{\underline{q}_o} = 4 \pi i \left(\frac{e^2 \hbar}{2 \gamma\, w_{\underline{q}_o} V} \right)^{\frac{1}{2}} \frac{1}{\underline{q}_o} \qquad (3.13a)$$

where $1/\gamma$ is given by (1.29); V is the volume of the crystal. Similarly, using the concept of deformation potential introduced in the earlier chapter, we can write[5]

$$A_{\underline{q}_a} = \left(\frac{\hbar}{2\, \rho\, w_{\underline{q}_a} V} \right)^{\frac{1}{2}} q_a\, \varepsilon_d \qquad (3.13b)$$

Therefore, the coefficients $P_{\underline{q}_o}$ and $A_{\underline{q}_a}$ depend on the model utilized in the development of the theory and the expressions (3.11) and (3.12) are purely formal in nature.

For the formal development of the theory, we shall use the form (3.11) and (3.12). Further, we assume that $P_{\underline{q}_o}$ and $A_{\underline{q}_a}$ can connect the atomic orbital states or Wannier functions of two bands either on the same atom or on the neighbouring atoms.

We now consider the eigen-functions of the electronic part of the Hamiltonian. Thus for the unperturbed problem we have

$$H_e \; \phi_{\underline{k}t} = E_{\underline{k}t} \; \phi_{\underline{k}t} \tag{3.14}$$

where

$$\phi_{\underline{k}t} = \frac{1}{\sqrt{V}} \; U_{\underline{k}t} \, e^{i \, \underline{k}\cdot\underline{r}} \tag{3.15}$$

as given by (1.4) except for the normalisation factor $1/\sqrt{V}$. Here, t is the band index and $\underline{k}$ is the propagation vector of the electron.

Let us consider the role of P. It is assumed that P is a small perturbation and can cause inter-band transitions of the charge carriers. Using the first order perturbation theory the solution of the equation

$$(H_e + P) \, \Psi_{\underline{k}} = E \Psi_{\underline{k}} \tag{3.16}$$

is taken as

$$\Psi_{\underline{k}} = \phi_{\underline{k}t} + \sum_{t'} P_{tt'} \; \phi_{\underline{k}t'} \tag{3.17}$$

where

$$p_{tt'} = \frac{\langle \phi_{\underline{k}'t'} \mid P \mid \phi_{\underline{k}t} \rangle}{\triangle E_{tt'}} \tag{3.18}$$

and $\triangle E_{tt'}$ is the energy denominator involved in the transition. A perturbation mixing of the states similar to (3.17) with the acoustical mode is perhaps not important in polar semiconductors.

The transport properties can be determined by solving the time - dependent Schrodinger's equation as given by (1.10) namely,

$$(H_o + H^1) \psi_{\underline{k}} = i \hbar \frac{\partial \psi_{\underline{k}}(t)}{\partial t} \tag{3.19}$$

where H_o is the Hamiltonian of the unperturbed problem and H^1 is a small perturbation which is taken to cause the scattering of the charge carriers.

<u>Scattering with acoustical modes</u>

First we consider the role of A in scattering the charge carriers from the state $\psi_{\underline{k}}$ to $\psi_{\underline{k}''}$. The matrix element of the scattering process is given by

$$\psi_{\underline{k}''} \quad A \quad \psi_{\underline{k}} \tag{3.20}$$

Using the form given by (3.17) for $\psi_{\underline{k}}$ and $\psi_{k''}$ we can write (3.20) as

$$\left\langle \psi_{\underline{k}''} \middle| A \middle| \psi_{\underline{k}} \right\rangle = \left\langle \phi_{\underline{k}''t} + \sum_{t''} P_{tt''} \phi_{k''t''} \middle| A \middle| \phi_{\underline{k}t} + \sum_{t'} P_{tt'} \phi_{\underline{k}'t'} \right\rangle$$

$$= \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}t} \right\rangle + \sum_{t''} P_{tt''} \left\langle \phi_{k''t''} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$+ \sum_{t'} \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle P_{tt'}$$

$$+ \sum_{t't''} P_{tt''} \left\langle \phi_{\underline{k}''t''} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle P_{tt'} \quad ..(3.21)$$

In proceeding further, we utilise the expressions (3.11), (3.12) and (3.15). Thus the first term in (3.21) can be written as

$$H_{int}(i) = \left\langle \phi_{k''t} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$= \sum_{q_a} \frac{1}{V} \left\langle U_{k''t} \, e^{i\underline{k}'' \underline{r}} \middle| A_{q_a} \left(b^*_{q_a} e^{-i \underline{q}_a \cdot \underline{r}} - b_{q_a} e^{iq\cdot\underline{r}} \right) \middle| U_{kt} e^{i\underline{k}\cdot\underline{r}} \right\rangle$$

$$\ldots\ldots\ldots(3.22)$$

The integration in the equation (3.22) should be carried out throughout the volume of the crystal using the fact that $U_{\underline{k}t}$'s possess the periodicity of the lattice. The integration appearing in (3.22) can be reduced to the integration over one unit cell and summation over all the cells. Thus the equation (3.22) can be written as

$$H_{int}(i) = \frac{1}{V} \sum_{q_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \sum_{r_j} \left(b^{*}_{q_a} e^{i(\underline{k}-\underline{k}''-\underline{q}_a)r_j} - b_{q_a} e^{-i(\underline{k}-\underline{k}''+\underline{q}_a)\cdot r_j} \right) \qquad \ldots(3.23)$$

where $\underline{r}_j$ runs over all the unit cells of the crystal. Now, we use the fact that the number of allowed values of the wave vectors is exactly equal to the number of unit cells in the whole crystal.

In simplifying the expression (3.23), we utilise the relation

$$\sum_{r_j} e^{i\,\underline{q}\cdot\underline{r}_j} \quad \begin{matrix} = 0 \\ = V \end{matrix} \quad \left.\begin{matrix} \\ \\ \end{matrix}\right\} \quad \begin{matrix} \underline{q} \neq g \\ \underline{q} = g \end{matrix} \qquad (3.24)$$

where $\underline{g}$ is an arbitrary vector of the reciprocal lattice including zero. Thus we get

$$\underline{k} - \underline{k}'' - \underline{q}_a = \underline{g}$$

$$\underline{k} - \underline{k}'' + \underline{q}_a = \underline{g}$$

when $\underline{g} = 0$ the process is known as "Normal process" and when $\underline{g} \neq 0$ it is known as "Umklapp process". It can be shown that for the semiconductor model chosen "umklapp processes" are not important. Thus we consider the case when $\underline{g} = 0$.

Therefore

$$H_{int}(i) = \sum_{q_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \left[b^{*}_{\underline{q}_a} \triangle(\underline{q}_a, \underline{k}-\underline{k}'') - b_{\underline{q}_a} \triangle(\underline{q}_a, \underline{k}''-\underline{k}) \right]$$

...........(3.25)

where the symbol $\triangle(x,y)$ is the well known Kronecker delta and

$$\triangle(x, y) = 1, \quad x = y$$

$$\triangle(x, y) = 0, \quad x \neq y$$

It follows from (3.25) that

$$\left.\begin{aligned} \underline{k} - \underline{k}'' - \underline{q}_a &= 0 \\ \underline{k} - \underline{k}'' + \underline{q}_a &= 0 \end{aligned}\right\} \qquad (3.26)$$

Similarly, one can write the other terms in (3.21) as

$$H_{int}(ii) = \sum P_{tt''} \left\langle \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$= \frac{1}{V^2} \sum_{\underline{q}_o, q_o, t''} \frac{\left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \left[(b^{*}_{\underline{q}_o} e^{i(\underline{k}'''-\underline{k}''-\underline{q}_o)\cdot\underline{r}} - b_{\underline{q}_a} e^{i(\underline{k}'''-\underline{k}''+\underline{q}_o)\cdot\underline{r}} \right] \middle| U_{\underline{k}''t''} \right\rangle}{\triangle E_{tt''}}$$

$$\left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \left[b^{*}_{\underline{q}_a} e^{i(\underline{k}-\underline{k}'''-\underline{q}_a)\cdot\underline{r}} - b_{\underline{q}_a} e^{i(\underline{k}-\underline{k}'''+\underline{q}_a)\cdot\underline{r}} \right] \middle| U_{\underline{k}t} \right\rangle$$

$$= \sum_{\underline{q}_o, \underline{q}_a t''} \frac{1}{\triangle E_{tt''}} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle$$

$$\times \left[b^{*}_{\underline{q}_o} \triangle(q_o, \underline{k}'''-\underline{k}'') - b_{\underline{q}_o} \triangle(\underline{q}_o, \underline{k}''-\underline{k}''') \right]$$

$$\times \left[b^{*}_{\underline{q}_a} \triangle(\underline{q}_a, \underline{k}-\underline{k}''') - b_{\underline{q}} \triangle(\underline{q}_a, \underline{k}'''-\underline{k}) \right]$$

.... (3.27)

The interference conditions from (3.27) are

$$\left.\begin{array}{lcl} \underline{k}''' - \underline{k}'' - \underline{q}_o = 0 & & \underline{k}''' - \underline{k}'' + \underline{q}_o = 0 \\ & \text{OR} & \\ \underline{k} - \underline{k}''' - \underline{q}_a = 0 & & \underline{k} - \underline{k}''' + \underline{q}_a = 0 \end{array}\right\} \qquad (3.28)$$

$$H_{int}(iii) = \sum \left\langle \phi_{\underline{k}''t} \right| A \left| \phi_{\underline{k}'t'} \right\rangle P_{tt'}$$

$$= \sum_{\underline{q}_o, \underline{q}_a t''} \frac{1}{\Delta E_{tt'}} \left\langle U_{\underline{k}''t} \right| A_{\underline{q}_a} \left| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \right| P_{\underline{q}_o} \left| U_{\underline{k}t} \right\rangle$$

$$\times \left[b^*_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}'-\underline{k}'') - b_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}''-\underline{k}') \right]$$

$$\times \left[b^*_{\underline{q}_o} \Delta(\underline{q}_o, \underline{k}-\underline{k}') - b_{\underline{q}_a} \Delta(\underline{q}_o, \underline{k}'-\underline{k}) \right]$$

$$\ldots\ldots\ldots \quad (3.29)$$

With the interference conditions, namely,

$$\left.\begin{array}{lcl} \underline{k} - \underline{k}'' - \underline{q}_a = 0 & & \underline{k}' - \underline{k}'' + \underline{q}_a = 0 \\ & \text{OR} & \\ \underline{k} - \underline{k}'' - \underline{q}_o = 0 & & \underline{k} - \underline{k}' + \underline{q}_o = 0 \end{array}\right\} \qquad (3.30)$$

$$H_{int}(iv) = \sum_{t't''} P_{tt''} \left\langle \phi_{\underline{k}'''t''} \right| A \left| \phi_{\underline{k}'t'} \right\rangle P_{tt'}$$

$$= \sum_{t',t''} \sum_{\underline{q}_o,\underline{q}_a,\underline{q}'_o} \left\langle U_{\underline{k}''t} \right| P_{\underline{q}_o} \left| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}''t''} \right| A_{\underline{q}_a} \left| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \right| P_{\underline{q}'_o} \left| U_{\underline{k}t} \right\rangle$$

$$\times \left[b^*_{\underline{q}_o} \Delta(\underline{q}_o, \underline{k}''' - \underline{k}'') - b_{\underline{q}_o} \Delta(\underline{q}_o, \underline{k}'' - \underline{k}''') \right]$$

$$\times \left[b^*_{\underline{q}_o} \Delta(\underline{q}_a, \underline{k}' - \underline{k}''') - b_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}''' - \underline{k}') \right]$$

$$\times \left[b^*_{q_o} \Delta(q'_o, \underline{k} - \underline{k}') - b_{q_o} \Delta(q'_o, \underline{k}' - \underline{k}) \right] \frac{1}{\Delta E_{tt''} \Delta E_{tt'}}$$

..............(3.31)

With the interference conditions, namely,

$$\left.\begin{array}{lll} \underline{k}''' - \underline{k}'' - \underline{q}_o = 0 & & \underline{k}''' - \underline{k}'' + \underline{q}_o = 0 \\ \underline{k}' - \underline{k}''' - \underline{q}_a = 0 & \text{OR} & \underline{k}' - \underline{k}''' + \underline{q}_a = 0 \\ \underline{k} - \underline{k}' - \underline{q}'_o = 0 & & \underline{k} - \underline{k}' + \underline{q}'_o = 0 \end{array}\right\} \qquad (3.32)$$

We write down the various interaction terms given above in a convenient form by introducing the second quantization representation for fermions with the creation ($a^*_{\underline{k}}$) and annihilation ($a_{\underline{k}}$) operators satisfying the relations.[61]

$$\left.\begin{array}{lll} a_{\underline{k}} a^*_{\underline{k}} + a^*_{\underline{k}} a_{\underline{k}} & = & \delta_{\underline{k}\,\underline{k}'} \\ a_{\underline{k}} a'_{\underline{k}} + a_{\underline{k}'} a_{\underline{k}} & = & 0 \\ a^*_{\underline{k}} a^*_{\underline{k}'} + a^*_{\underline{k}'} a^*_{\underline{k}} & = & 0 \end{array}\right\}$$

and utilising the various interference conditions related to the conservations of propagation vectors. In this new representations, the interaction terms, namely, (3.25), (3.27), (3.29) and (3.31) become

$$H_{int}(i) = \sum_{\underline{q}_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \Big[a^{*}_{\underline{k}-\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}+\underline{q}_a}\, a_{\underline{k}} b_{\underline{q}_a} + \text{c.c} \Big] \qquad \ldots(3.33a)$$

where c.c. denotes complex conjugate term of the preceding terms.

$$H_{int}(ii) = \sum_{t''} \sum_{\underline{q}_o,\underline{q}_a} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \frac{1}{\Delta E_{tt''}}$$
$$\times \Big[a^{*}_{\underline{k}-\underline{q}_o-\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_o}\, b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}-\underline{q}_o+\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_o}\, b_{\underline{q}_a}$$
$$- a^{*}_{\underline{k}+\underline{q}_o-\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_o}\, b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}+\underline{q}_o+\underline{q}_a}\, a_{\underline{k}}\, b_{\underline{q}_o}\, b_{\underline{q}_a} + \text{c.c.} \Big]$$
$$\ldots(3.33b)$$

$$H_{int}(iii) = \sum_{t'} \sum_{q_o,q_a} \left\langle U_{\underline{k}''t} \middle| A_{q_a} \middle| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \middle| P_{q_o} \middle| U_{\underline{k}t} \right\rangle \frac{1}{\Delta E_{tt'}}$$
$$\times \Big[a^{*}_{\underline{k}-\underline{q}_o-\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_o}\, b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}+\underline{q}_o-\underline{q}_a}\, a_{\underline{k}}\, b_{\underline{q}_o}\, b^{*}_{\underline{q}_a}$$
$$- a^{*}_{\underline{k}-\underline{q}_o+\underline{q}_a}\, a_{\underline{k}}\, b^{*}_{\underline{q}_o}\, b_{\underline{q}_o} + a^{*}_{\underline{k}+\underline{q}_o+\underline{q}_a}\, a_{\underline{k}}\, b_{\underline{q}_o} b_{\underline{q}_a} + \text{c.c.} \Big]$$
$$\ldots(3.33c)$$

$$H_{int}(iv) = \sum_{t',t''} \sum_{q_o,q_a,q_o'} , \frac{1}{\triangle E_{tt''} \triangle E_{tt'}}$$

$$\times \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \middle| P_{\underline{q}_o'} \middle| U_{\underline{k}t} \right\rangle$$

$$\times \Big[a^*_{\underline{k}-\underline{q}_o-\underline{q}_a-\underline{q}_o'} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}_a} b^*_{\underline{q}_o'} - a^*_{\underline{k}+\underline{q}_o+\underline{q}_a+\underline{q}_o'} a_{\underline{k}} b_{\underline{q}_o} b_{\underline{q}_a} b_{\underline{q}_o'}$$

$$+ a^*_{\underline{k}+\underline{q}\ +\underline{q}\ -\underline{q}'} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}_a} b^*_{\underline{q}_o'} - a^*_{\underline{k}-\underline{q}_o+\underline{q}_a-\underline{q}_o'} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}_a} b^*_{\underline{q}_o'}$$

$$- a^*_{\underline{k}+\underline{q}_o-\underline{q}_a-\underline{q}_o'} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}_a} b^*_{\underline{q}_o} - a^*_{\underline{k}-\underline{q}_o-\underline{q}_a+\underline{q}_o'} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}_a} b_{\underline{q}_o'}$$

$$+ a^*_{\underline{k}-\underline{q}_o+\underline{q}_a+\underline{q}_o'} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}_a} b_{\underline{q}_o'} + a_{\underline{k}-\underline{q}_o-\underline{q}_a+\underline{q}_o'} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}_a} b_{\underline{q}_o'}$$

$$+ \text{c. c.} \Big] \qquad \text{.....(3.33d)}$$

<u>Scattering with optical modes:</u>

In what follows, we shall take up the role of optical mode interaction in the scattering processes of the electron from the state $\Psi_{\underline{k}}$ to $\Psi_{\underline{k}''}$. The matrix element of the scattering processes is given by

$$\langle \Psi_{\underline{k}''} | P | \Psi_{\underline{k}} \rangle$$

$$= \left\langle \phi_{\underline{k}''t} + \sum_{t''} P_{tt''} \phi_{\underline{k}'''t''} \middle| P \middle| \phi_{\underline{k}t} + \sum_{t'} P_{tt'} \phi_{\underline{k}'t'} \right\rangle$$

$$= \langle \phi_{\underline{k}''t} | P | \phi_{\underline{k}t} \rangle + \sum_{t''} P_{tt''} \langle \phi_{\underline{k}'''t''} | P | \phi_{\underline{k}t} \rangle$$

$$+ \sum_{t'} \langle \phi_{\underline{k}''t} | P | \phi_{\underline{k}'t'} \rangle P_{tt'} + \sum_{t''t'} P_{tt''} \langle \phi_{\underline{k}'''t''} | P | \phi_{\underline{k}'t'} \rangle P_{tt'}$$

.... (3.34)

Let us consider the first term in (3.34). This can be written in the second quantization representation, as done earlier for the acoustical case, as

$$H'_{int}(i) = \left\langle \phi_{\underline{k}''t} \middle| P \middle| \phi_{\underline{k}t} \right\rangle$$

$$= \sum_{q_o} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}t} \right\rangle \left[a^*_{\underline{k}-\underline{q}_o} a_{\underline{k}} b^*_{\underline{q}_o} - a^*_{\underline{k}+\underline{q}_o} a_{\underline{k}} b_{\underline{q}_o} + c.c. \right] \qquad \ldots\ldots (3.35a)$$

Here we see that the interaction term has the same form as (3.33a) except for $P_{\underline{q}_o}$ in place of $A_{\underline{q}_a}$ and momentum vector of the optical modes instead of the acoustical mode. Similarly, we can write down the other terms in (3.34) as follows:

$$H'_{int}(ii) =$$

$$= \sum_{t'', q_o, q'_o} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \middle| P_{q'_o} \middle| U_{\underline{k}t} \right\rangle \frac{1}{\Delta E_{tt'}}$$

$$\times \left[a^*_{\underline{k}-\underline{q}_o-\underline{q}'_o} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}'_o} - a^*_{\underline{k}-\underline{q}_o+\underline{q}'_o} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}'_o} \right.$$

$$\left. - a^*_{\underline{k}+\underline{q}_o-\underline{q}'_o} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}'_o} + a^*_{\underline{k}+\underline{q}_o+\underline{q}'_o} a_{\underline{k}} b_{\underline{q}_o} b_{\underline{q}'_o} + c.c. \right] \qquad \ldots\ldots\ldots\ldots (3.35b)$$

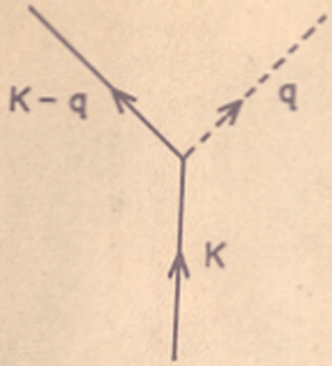


Fig. 1·a

Fig. 1·b

ONE PHONON PROCESSES

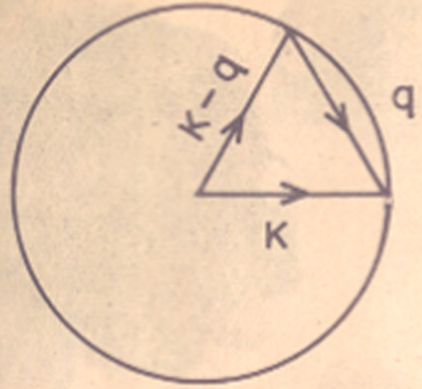


Fig. 3·a

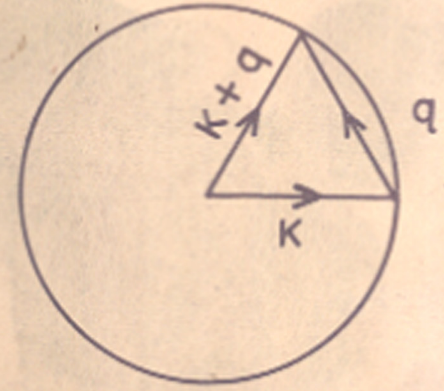


Fig. 3·b

SCATTERING PROCESSES (NORMAL PROCESSES - ONE PHONON PROCESSES) ON A CONSTANT ENERGY SURFACE.

$$
\begin{aligned}
H'_{int}(iii) = \sum_{t'} \sum_{\underline{q}_o,\underline{q}'_o} & \left\langle U_{\underline{k}''t} \right| \rho_{q'_o} \left| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \right| \rho_{\underline{q}_o} \left| U_{\underline{k}t} \right\rangle \frac{1}{\Delta E_{tt'}} \\
& \times \Big[a^*_{\underline{k}-\underline{q}_o-\underline{q}'_o} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}'_o} - a^*_{\underline{k}+\underline{q}_o-\underline{q}'_o} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}'_o} \\
& - a^*_{\underline{k}-\underline{q}_o+\underline{q}'_o} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}'_o} + a^*_{\underline{k}+\underline{q}_o+\underline{q}'_o} a_{\underline{k}} b_{\underline{q}_o} b_{\underline{q}'_o} + c.c. \Big]
\end{aligned}
$$

.... (3.35c)

$$
\begin{aligned}
H'_{int}(iv) = \sum_{t't''} \sum_{q_o q'_o q''_o} & \frac{1}{\Delta E_{tt''} \Delta E_{tt'}} \\
& \times \left\langle U_{\underline{k}''t} \right| \rho_{\underline{q}_o} \left| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \right| \rho_{\underline{q}'_o} \left| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \right| \rho_{\underline{q}''_o} \left| U_{\underline{k}t} \right\rangle \\
& \times \Big[a^*_{\underline{k}-\underline{q}_o-\underline{q}'_o-\underline{q}''_o} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}'_o} b^*_{\underline{q}''_o} - a^*_{\underline{k}+\underline{q}_o+\underline{q}'_o+\underline{q}''_o} a_{\underline{k}} b_{\underline{q}_o} b_{\underline{q}'_o} b_{\underline{q}''_o} \\
& + a^*_{\underline{k}+\underline{q}_o+\underline{q}'_o-\underline{q}''_o} a_{\underline{k}} b_{\underline{q}_o} b_{\underline{q}'_o} b^*_{\underline{q}''_o} - a^*_{\underline{k}-\underline{q}_o+\underline{q}'_o-\underline{q}''_o} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}'_o} b^*_{\underline{q}''_o} \\
& - a^*_{\underline{k}+\underline{q}_o-\underline{q}'_o-\underline{q}''_o} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}'_o} b^*_{\underline{q}''_o} - a^*_{\underline{k}-\underline{q}_o-\underline{q}'_o+\underline{q}''_o} a_{\underline{k}} b^*_{\underline{q}_o} b^*_{\underline{q}'_o} b_{\underline{q}''_o} \\
& + a^*_{\underline{k}-\underline{q}_o+\underline{q}'_o+\underline{q}''_o} a_{\underline{k}} b^*_{\underline{q}_o} b_{\underline{q}'_o} b_{\underline{q}''_o} - a^*_{\underline{k}+\underline{q}_o-\underline{q}'_o-\underline{q}''_o} a_{\underline{k}} b_{\underline{q}_o} b^*_{\underline{q}'_o} b^*_{\underline{q}''_o} \\
& + c.\ c. \Big]
\end{aligned}
$$

.... (3.35d)

Let us consider the various terms given in (3.33) and (3.35). The terms numbered as (a) describe one phonon processes and are represented in Figs(1 &3), where the momentum vector $\underline{q}$

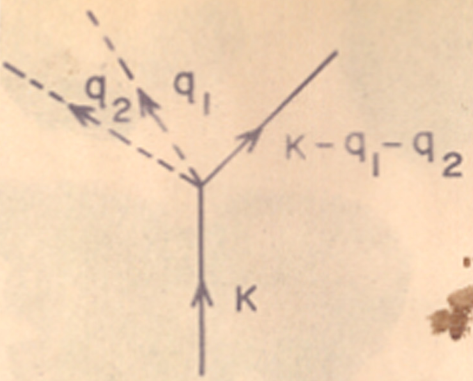


Fig. 2·a

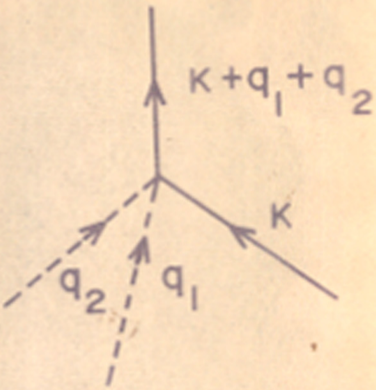


Fig. 2·b

Fig. 2·c

Fig. 2·d

TWO PHONON PROCESSES

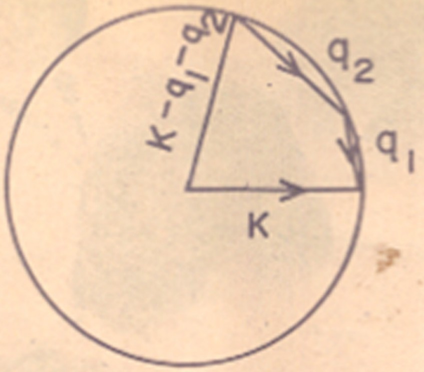


Fig. 4·a

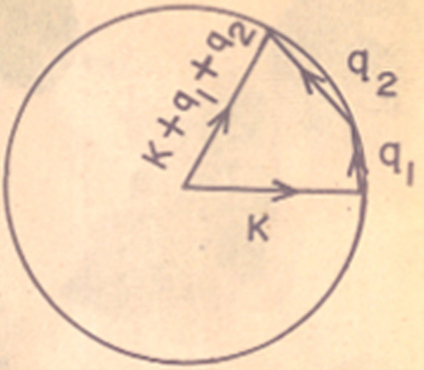


Fig. 4·b

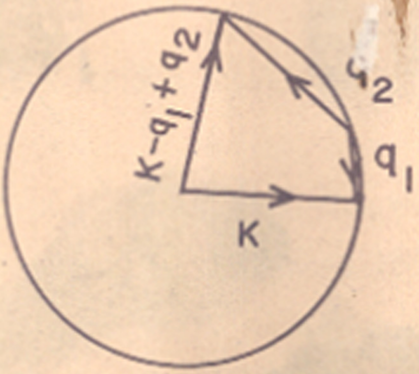


Fig. 4·c

Fig. 4·d

SCATTERING PROCESSES (NORMAL PROCESSES - TWO PHONON PROCESSES) ON A CONSTANT ENERGY SURFACE.

denotes either an optical or an acoustic phonon. The solid line in the diagram represents an electron and the broken line a phonon. Here, in the scattering process, an electron makes a transition from a state $\underline{k}$ to $\underline{k} \pm \underline{q}$ by emission or absorption of a phonon of wave vector $\underline{q}$.

The terms (b) and (c) describe two phonon processes and are represented in Figs.(2 & 4). Here, the electron undergoes an interband transition by emitting or absorbing an optical phonon and it is scattered by emission or absorption of an acoustic (3.33b,c) or optical phonon (3.35b,c)

The terms (d) describe three phonon processes. These processes are not considered in the present investigation.

(2) PbS group, Solid Solutions[60]

In the preceding section, we have formulated the interaction Hamiltonian for pure PbS like systems. In what follows, we formulate the interaction Hamiltonian for the case of the solid solution of PbS group. It is known that solid solutions of homogeneous composition with the crystal structure isomorphous with MX exist. Further we assume that the anions in the solid solution are arranged in a random manner over the anion sites. For the formal development of the theory, the system $MX_{1-f}\,Y_f$ is selected, where M is the metal ion and X and Y represent the anions; f denotes the concentration of Y ions.

The total Hamiltonian for the one electron problem is

$$H = -\frac{\hbar^2\nabla^2}{2m} + \sum_m V_m(\underline{r}-\underline{R}_m^o) + \sum_x V_x(\underline{r}-\underline{R}_x^o) + \sum_y V_y(\underline{r}-\underline{R}_y^o) + H_{eL} + H_L \qquad \ldots\ldots\ldots\ldots\ldots(3.36)$$

where $-\frac{\hbar^2\nabla^2}{2m}$ is the kinetic energy operator; $\sum_m V_m(\underline{r}-\underline{R}_m^o)$ is the potential at the electron due to the metal ions at equilibrium position and $\sum_{x,y} V_{x,y}(\underline{r}-\underline{R}_{x,y}^o)$ represent the same due to the anions. H_{eL} is the electron lattice interaction Hamiltonian. H_L is the lattice Hamiltonian expressed as in (1.16) and (3.4). In proceeding further, we shall first take an average potential at all anions which may be represented as[4,26]

$$\sum_l \sum_s f_s V_s(\underline{r}-\underline{R}_l^o) = \sum_l V_1(\underline{r}-\underline{R}_l^o) \qquad (3.37)$$

where f_s is the concentration of s type atom in the lattice.

Now the difference:

$$V^{(p)} = \sum_{x,y} V_{x,y}(\underline{r}-\underline{R}_{x,y}^o) - \sum_l \sum_s f_s V_s(\underline{r}-\underline{R}_l^o) \qquad (3.38)$$

is treated as the perturbation which arises as a result of alloying effect. The total periodic potential can be expressed as

$$V(\underline{r}) = \sum_m V_m(\underline{r}-\underline{R}_m^o) + \sum_l V_1(\underline{r}-\underline{R}_l^o) \qquad (3.39)$$

With these definitions the Hamiltonian (3.36) becomes

$$H = H_o + V^{(p)} + H_{eL} + H_L \qquad (3.40)$$

Here $H_o = -\hbar^2\nabla^2/2m + V(\underline{r})$ is treated as the unperturbed Hamiltonian. The eigen functions $\phi_{\underline{k}t}$ and eigen-values $E_{\underline{k}t}$ of the Hamiltonian H_o ~~is~~ are given by the equation

$$H_o\phi_{\underline{k}t} = E_{\underline{k}t}\phi_{\underline{k}t} \qquad (3.41)$$

$$\phi_{\underline{k}t} = (1/\sqrt{V})U_{\underline{k}t}\, e^{i\underline{k}\cdot\underline{r}} \qquad (3.42)$$

As in the previous section the electron-lattice interaction term can be written as

$$H_{eL} = P + A \qquad (3.43)$$

where P and A are given by (3.11) and (3.12). We now consider $V^{(p)}$ as a small perturbation causing inter-band transition of the charge carriers. A mixing of Bloch~~'s~~ functions may be possible and such a mixing was invoked earlier for Ge-Si alloys.[62] However no explicit calculation was reported. We can show on a simple crystal field model (see appendix) that the alloying effect can indeed cause such transitions. Let us consider as an example a Pb^{++} ion surrounded by an octahedron of ligands say six Se^{--}. If we replace one Se^{--} by one Te^{--} then the perturbations $V_{lm}^{(p)}$ for this unit can be expressed as

$$V_{1m}^{(p)} = \frac{Q' + 5Q}{R_h} + (Q' - Q)\left(\frac{z}{R_h^2} + \frac{3z^2 - r^2}{2R_h^3} + \dots\right) \qquad (3.44)$$

where Q' is the effective charge of the impurity ion and Q that of the virtual anion; z, r are the co-ordinates of the electron around the central ion (Pb^{++}) and R_h is the inter-ionic distance. It can be seen that (3.44) admixes atomic s states with p or d states. Here (3.44) acts as a small perturbation at the site of the metal ion. Similarly, we can have perturbation at the anion site. We assume that all these perturbations are included in $V^{(p)}$.

Thus, we can write down the equation of perturbed problem as

$$(H_o + V^{(p)})\,\Psi_{\underline{k}} = E\Psi_{\underline{k}} \qquad (3.45)$$

where

$$\Psi_{\underline{k}} = \phi_{\underline{k}t} + \sum_{t'} V_{tt'}^{(p)}\ \phi_{\underline{k}'t'} \qquad (3.46)$$

and
$$V_{tt'}^{(p)} = \frac{\langle \phi_{\underline{k}t} |\ V^{(p)} |\ \phi_{\underline{k}'t'} \rangle}{\Delta E_{tt'}} \qquad (3.47)$$

In proceeding further, we consider the role of acoustic mode of vibration in the scattering process. The role of optical modes of vibration seems to be unimportant as we are interested in the low temperature region ($T > 50^\circ K$). The matrix element of the scattering process is given by

$$\left\langle \psi_{\underline{k}''} \middle| A \middle| \psi_{\underline{k}} \right\rangle$$

$$= \left\langle \phi_{\underline{k}''t} + \sum_{t''} V^{(p)}_{tt''} \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}t} + \sum_{t'} V^{(p)}_{t't} \phi_{\underline{k}'t'} \right\rangle$$

$$= \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}t} \right\rangle + \sum_{t''} V^{(p)}_{tt''} \left\langle \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$+ \sum_{t'} \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle V^{(p)}_{t't}$$

$$+ \sum_{t''t'} V^{(p)}_{t''t} \left\langle \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle V^{(p)}_{t't} \qquad ..(3.48)$$

We shall now consider the various terms in (3.48) separately. In simplifying these terms, we utilize the expressions (3.38), (3.42) and (3.12). The first term of (3.48) then becomes

$$H'_{int}(i) = \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$= \sum_{\underline{q}_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \left[b^*_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}-\underline{k}'') - b_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}''-\underline{k}) \right]$$

$$= \sum_{\underline{q}_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \left[a^*_{\underline{k}-\underline{q}_a} a_{\underline{k}} b^*_{\underline{q}_a} - a^*_{\underline{k}+\underline{q}_a} a_{\underline{k}} b_{\underline{q}_a} + c.c. \right]$$

$$\qquad .... (3.49a)$$

The second term

$$H'_{int}(ii) = \sum_{t''} V^{(p)}_{tt''} \left\langle \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}t} \right\rangle$$

$$= \sum_{t''q_a} \left\langle U_{\underline{k}''t} \middle| \sum_{n} \frac{\left\{ V_n(\underline{r}-\underline{R}_n^o) - \sum_{s} f_s V_s(\underline{r}-\underline{R}_n^o) \right\} \Delta(\underline{k}''', \underline{k}'')}{\Delta E_{tt''}} \middle| U_{\underline{k}'''t''} \right\rangle$$

$$\left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \left\{ \Delta(\underline{q}_a, \underline{k}-\underline{k}''') b^*_{\underline{q}_a} - b_{\underline{q}_a} \Delta(\underline{q}_a, \underline{k}'''-\underline{k}) \right\} \middle| U_{\underline{k}t} \right\rangle$$

$$= \sum_{t''\underline{q}_a} \frac{V^{(p)}_{\underline{k}''t, \underline{k}'''t''}}{\Delta E_{tt''}} \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle$$

$$\left[a^*_{\underline{k}-\underline{q}_a} a_{\underline{k}} b^*_{\underline{q}_a} - a^*_{\underline{k}+\underline{q}_a} a_{\underline{k}} b_{\underline{q}_a} + c.\ c. \right] , \quad \ldots.(3.49b)$$

where

$$\frac{V^{(p)}_{\underline{k}''t, \underline{k}'''t''}}{\Delta E_{tt''}} = \left\langle U_{\underline{k}''t} \middle| \sum_{n} \left\{ V_n(\underline{r}-\underline{R}_n^o) - \sum_{S} f_s V_s(\underline{r}-\underline{R}_n) \right\} \middle| U_{\underline{k}'''t''} \right\rangle$$

$$\ldots.(3.49b')$$

Similarly the third and the fourth terms in (3.48) can be expressed in the same notation as (3.49b)

$$H'_{int}(iii) = \sum_{t'} \left\langle \phi_{\underline{k}''t} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle V^{(p)}_{t't}$$

$$= \sum_{t', q_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}'t'} \right\rangle \frac{V^{(p)}_{\underline{k}'t', \underline{k}t}}{\Delta E_{tt'}}$$

$$\left[a^*_{\underline{k}-q_a} a_{\underline{k}} b^*_{\underline{q}_a} - a^*_{\underline{k}+\underline{q}_a} a_{\underline{k}} b_{\underline{q}_a} + c.c. \right] \quad \ldots.(3.49c)$$

$$H'_{int}(iv) = \sum_{t't''} V^{(p)}_{tt''} \left\langle \phi_{\underline{k}'''t''} \middle| A \middle| \phi_{\underline{k}'t'} \right\rangle V^{(p)}_{t't}$$

$$= \sum_{t',t'',\underline{q}_a} \frac{V^{(p)}_{\underline{k}t,\underline{k}'''t''}}{\triangle E_{tt''}} \left\langle U_{\underline{k}'''t''} \middle| A_{q_a} \middle| U_{\underline{k}'t'} \right\rangle \frac{V^{(p)}_{\underline{k}'t',\underline{k}t}}{\triangle E_{tt'}}$$

$$\left[a^{*}_{\underline{k}-\underline{q}_a} a_{\underline{k}} b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}+\underline{q}_a} a_{\underline{k}} b_{\underline{q}_a} + c.c. \right] \qquad ....(3.49d)$$

In writing down the various interaction terms (3.49d) we have utilized the relevant interference conditions for the wave vectors of the electrons and phonons under considerations. These are:

$$\underline{k}'' = \underline{k} \pm q_a \qquad (3.50a)$$

$$\underline{k}'' = \underline{k}''' \quad ; \quad \underline{k}'' = \underline{k} \pm \underline{q}_a \qquad (3.50b)$$

$$\underline{k}' = \underline{k} \quad ; \quad \underline{k}' = \underline{k}'' \pm \underline{q}_a \qquad (3.50c)$$

$$\left.\begin{array}{l} \underline{k}''' = \underline{k}'' \\ \underline{k} = \underline{k}' \end{array}\right\} \quad \underline{k}' = \underline{k}''' \pm q_a \qquad (3.50d)$$

Thus we can write

$$H_{int} = H'_{int}(i) + H'_{int}(ii) + H'_{int}(iii) + H'_{int}(iv)$$

$$= \sum_{q_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle + \sum_{t''} \frac{V^{(p)}_{\underline{k}'',t;\underline{k}'''t''}}{\triangle E_{tt''}} \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle$$

$$+ \sum_{t'} \left\langle U_{k''t} \middle| A_{q_a} \middle| U_{k't'} \right\rangle \frac{V^{(p)}_{\underline{k}'t',\underline{k}t}}{\triangle E_{tt'}}$$

$$+ \sum_{t't''} \frac{V^{(p)}_{\underline{k}''t,\underline{k}'''t''}}{\triangle E_{tt''}} \left\langle U_{k'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}'t'} \right\rangle \frac{V^{(p)}_{\underline{k}'t',\underline{k}t}}{\triangle E_{tt'}}$$

$$\left[a^{*}_{\underline{k}-\underline{q}_a} a_{\underline{k}} b^{*}_{\underline{q}_a} - a^{*}_{\underline{k}+\underline{q}_a} a_{\underline{k}} b_{\underline{q}_a} + c.c. \right] \qquad .... (3.51)$$

Here all the terms describe one phonon process and can be represented by the same diagram (Figs.1 & 3) as given earlier. The first term represents scattering of Bloch electrons by acoustical phonons in the same band. The second and the third terms are the product of processes involving inter-band scattering owing to the crystal field perturbation $V^{(p)}$ and acoustical phonons. These are second order terms. The last term is a third order perturbation and it is believed to be unimportant. In the present investigation, we confine our attention to the first three terms.

Before concluding this section, it is expedient to write down the diagonal part of both the electron and lattice Hamiltonians in the second quantization representation as

$$H_o = H_e + H_L$$

$$H_o = \sum_{\underline{k},t} E_{\underline{k}t} \, a^*_{\underline{k}\sigma} a_{\underline{k}\sigma} + \sum_{\underline{q}} \hbar w_{\underline{q}} \, (b^*_{\underline{q}} b_{\underline{q}} + \tfrac{1}{2}), \qquad (3.52)$$

with $E_{\underline{k}t} = \hbar^2 k^2 / 2m^*$ as given by (1.5); m^* being the effective mass of the carriers and σ is the spin index for the spin states. The various operators occurring in (3.42), (3.35) and (3.51) connect the various eigen-states of the Hamiltonian (3.52). In the occupation number representation these eigen-states are denoted by

$$\left| \; \cdots \; n_{\underline{k}t} \cdots ; \; N_{\underline{q}p} \cdots \; , \right\rangle \qquad (3.53)$$

where $n_{\underline{k},t}$ and $N_{\underline{q}p}$ have the usual meaning given in the earlier chapter.

It is expedient to note the eigen values of the electron and the phonon creation and annihilation operators given by[63]

$$a^{*}_{\underline{k}} \left| \; \ldots n_{\underline{k}} \ldots \right\rangle = \theta_{\underline{k}}\, n_{\underline{k}} \left| \ldots, 1-n_{\underline{k}}, \ldots \right\rangle$$

$$a^{*}_{\underline{k}} \left| \; \ldots n_{\underline{k}} \ldots \right\rangle = \theta_{\underline{k}}(1-n_{\underline{k}}) \left| \ldots, 1-n_{\underline{k}}, \ldots \right\rangle$$

$$b^{*}_{\underline{q}p} \left| \; \ldots N_{\underline{q}p} \ldots \right\rangle = (N_{\underline{q}p}+1)^{\frac{1}{2}} \left| \ldots, N_{\underline{q}p}+1, \ldots \right\rangle$$

$$b_{\underline{q}p} \left| \; \ldots N_{\underline{q}p} \ldots \right\rangle = N_{\underline{q}p}^{\;\frac{1}{2}} \left| \ldots, N_{\underline{q}p}-1, \ldots \right\rangle \qquad \ldots\ldots\ldots (3.54)$$

~~respectively~~. Here $\theta_{\underline{k}} = (-1)^{\nu_k}$, $\nu_{\underline{k}} = \sum_{j=1}^{k-1} n_j$.

$\left| \ldots n_{\underline{k}} \ldots \right\rangle$ and $\left| \ldots N_{\underline{q}p} \ldots \right\rangle$ are the electron and phonon state functions respectively in the occupation number representation.

B. RELAXATION TIME AND MOBILITY

In the foregoing section, we have formulated the interaction Hamiltonian for the various interaction mechanisms for the transport problem. In order to solve the mobility problem it is usual to assume that a relaxation time exists for the processes described by the interaction Hamiltonian formulated in the previous chapter. Hence, we recall the definition of the relaxation time (1.19) namely,

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{net}} = - \frac{n_{\underline{k}} - n^{o}_{\underline{k}}}{\tau} . \qquad (3.55)$$

For the system under consideration, it can be shown that (3.55) remains valid. The solution of the Boltzmann transport equation is then straight forward and τ can be calculated. For simplicity, we shall assume that the applied field is in the x-direction.[64] Thus we can write the perturbed distribution function as

$$n_{\underline{k}} = n^{o}_{\underline{k}} + \frac{\hbar}{m^{*}} \, k_x \, \chi_{\underline{k}} \qquad (3.56)$$

where k_x is the x - component of the wave vector $\underline{k}$ and $\chi_{\underline{k}}$ is a small correction factor to the equilibrium distribution function $n^{o}_{\underline{k}}$

Also, we note that $\chi_{\underline{k}} = \chi(E_{\underline{k}})$.

Substituting (3.56) in (3.55) we get

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{net}} = - \frac{\hbar}{m^{*}} \frac{\underline{k}_x}{\tau} \qquad (3.57)$$

<u>PbS Group</u>:[56] We shall now calculate the rate of change of charge carrier distribution function due to the collision mechanism. From the expression (1.20) it is clear that the calculation of $\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{coll}}$ will inturn involve the calculation of the transition probabilities of the various processes enumerated in the earlier section.

Let us consider the interaction terms given by the expression (3.33). The calculation of the process (3.33a) i.e. the scattering of electrons with acoustical phonon have been reported elsewhere.[4,5] As remarked earlier such processes do not seem to be important for the systems under consideration in the high temperature region. Therefore we confine our attention to the terms (3.33b) and (3.33c). As a simplifying assumption, we restrict ourselves to the case of a two band model, namely t and t'.

Now, we can write down the net rate of change of distribution function for the charge carriers by substituting for the square of the matrix element of the interaction terms in the equation (1.20) as,

$$
\begin{aligned}
\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{net}} = \frac{2\pi}{\hbar} \sum_{\underline{q}_o,\underline{q}_a} & \left| P^{o}_{tt'} \; A^{a}_{t't} \right|^{2} \\
\times \Big\{ & \Big[(1-n_{\underline{k}})(n_{\underline{k}+\underline{q}_a+\underline{q}_a})(N_{\underline{q}_o}+1)(N_{\underline{q}_a}+1)-(n_{\underline{k}})(1-n_{\underline{k}+\underline{q}_o+\underline{q}_a})(N_{\underline{q}_o})(N_{\underline{q}_a}) \Big] \\
& \quad \times \delta\left(E_{\underline{k}+\underline{q}_o+\underline{q}_a}-E_{\underline{k}} - \hbar\,(w_{\underline{q}_o}+w_{\underline{q}_a})\right) \\
+ & \Big[(1-n_{\underline{k}})(n_{\underline{k}-\underline{q}_o-\underline{q}_a})(N_{\underline{q}_o})(N_{\underline{q}_a})-(n_{\underline{k}})(1-n_{\underline{k}-\underline{q}_o-\underline{q}_a})(N_{\underline{q}_o}+1)(N_{\underline{q}_a}+1) \Big] \\
& \quad \times \delta\left(E_{\underline{k}-\underline{q}_o-\underline{q}_a}- E_{\underline{k}} + \hbar\,(w_{\underline{q}_o}+w_{\underline{q}_a})\right) \\
+ & \Big[(1-n_{\underline{k}})(n_{\underline{k}-\underline{q}_o+\underline{q}_a})(N_{\underline{q}_o})(N_{\underline{q}_a}+1)-(n_{\underline{k}})(1-n_{\underline{k}-\underline{q}_o+\underline{q}_a})(N_{\underline{q}_o}+1)(N_{\underline{q}_a}) \Big] \\
& \quad \times \delta\left(E_{\underline{k}-\underline{q}_o+\underline{q}_a} - E_{\underline{k}} + \hbar(w_{\underline{q}_o} - w_{\underline{q}_a})\right)
\end{aligned}
$$

$$+\left[(1-n_{\underline{k}})(n_{\underline{k}+\underline{q}_o-\underline{q}_a})(N_{\underline{q}_o}+1)(N_{\underline{q}_a})-n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_o-\underline{q}_a})(N_{\underline{q}_o})(N_{\underline{q}_a}+1)\right]$$

$$\times\ \delta\left(E_{\underline{k}+\underline{q}_o-\underline{q}_a}-E_{\underline{k}}-\hbar\,(w_{\underline{q}_o}-w_{\underline{q}_a})\right)\Big\} \quad \ldots\ldots(3.58)$$

This expression involves the net rate of change of $n_{\underline{k}}$ owing to all types of processes described by (3.33b) and (3.33c). This is easily seen from the four types of δ- functions occurring in (3.58). Also, in (3.58) the factor

$$\left|P^{o}_{tt'}\,A^{a}_{t't}\right| = \frac{\langle U_{\underline{k}''t}\,|\,P_{\underline{q}_o}\,|\,U_{\underline{k}'''t'}\rangle}{\Delta E_{tt'}}\,\langle U_{\underline{k}'''t'}\,|\,A_{\underline{q}_a}\,|\,U_{\underline{k}t}\rangle$$

will depend on the model chosen for the calculation. In proceeding further, we change the summation over q_a to an integration as

$$\sum_{\underline{q}_a}\rightarrow\frac{V}{8\pi^3}\int d\underline{q}_a = \frac{V}{8\pi^3}\int q_a^2\,dq_a\,\sin\theta_{a\underline{k}}\,d\phi_{a\underline{k}} \quad \ldots\ldots(3.59)$$

Here, $(q_a, \theta_{a\underline{k}}, \phi_{a\underline{k}})$ are the polar coordinates. The integration over the angle $\theta_{a\underline{k}}$ can be performed using the properties of the δ-functions occurring in the expression (3.58). Let us consider the function

$$\delta\left(E_{\underline{k}+\underline{q}_o+\underline{q}_a}-E_{\underline{k}}-\hbar\,(w_{\underline{q}_o}+w_{\underline{q}_a})\right)$$

This implies

$$E_{\underline{k}+\underline{q}_o+\underline{q}_a}-E_{\underline{k}}-\hbar\,(w_{\underline{q}_o}+w_{\underline{q}_a}) = 0$$

This can be further simplified as

$$\frac{\hbar^2}{2m^*}\left[q_o^2 + q_a^2 + 2kq_o \operatorname{Cos} \theta_{\underline{k}o} + 2kq_o \operatorname{Cos} \theta_{\underline{k}o} + 2q_a q_o \operatorname{Cos} \theta_{ao} - \frac{2m^*}{\hbar}\left(w_{\underline{q}_o} + w_{\underline{q}_a} \right)\right] = 0$$

$$\frac{\hbar^2 k q_a}{m^*}\left[\frac{q_a}{2k} + \operatorname{Cos} \theta_{a\underline{k}} - \frac{m^*}{\hbar k q_a}\left(w_{\underline{q}_o} + w_{\underline{q}_a} \right)\right] = 0 \qquad \ldots(3.60)$$

where $\theta_{\underline{k}o}$ is the angle between q_o and $\underline{k}$. In arriving at (3.60) we have made use of the relation (1.5) and neglected the terms such as q_o^2, $2q_o q_a \operatorname{Cos} \theta_{ao}$, and $2\, kq_o \operatorname{Cos} \theta_{\underline{k}o}$ in as much as we always take very small values of q_o and the direction $\underline{q}_o$ is nearly normal to $\underline{k}$ vector. Further $\underline{q}_o$ is taken along the polar axis. The last term in (3.60), namely, $\frac{m^*}{\hbar\, k\, q_a} w_{\underline{q}_a}$ can be neglected, if we note that

$$\frac{m^* w_{\underline{q}_a}}{\hbar\, k\, q_a} = \frac{m^* c q_a}{\hbar\, k\, q_a} = c/v. \qquad (3.61)$$

where c and v are the velocities of sound and of electron respectively. This is supported by the fact that $v \gg c$ in the temperature region of our interest,[64] since the velocity of sound is of the order 5×10^5 cm/sec. and that of the electron $5.5 \times 10^5\, T^{\frac{1}{2}}$ cm/sec. Hence, from (3.60) we get

$$\operatorname{Cos} \theta_{ak}(i) = \frac{m^* w_{\underline{q}_o}}{\hbar\, k\, q_a} - \frac{q_a}{2k} \qquad (3.62)$$

Similarly the other δ-functions in (3.58) give the following relations

$$\left.\begin{aligned}\operatorname{Cos}\theta_{a\underline{k}}\ (ii) &= \frac{m^{*}\,w_{\underline{q}_o}}{\hbar\,k\,q_a} + \frac{q_a}{2k}\\[2ex] \operatorname{Cos}\theta_{a\underline{k}}\ (iii) &= -\frac{m^{*}\,w_{\underline{q}_o}}{\hbar\,k\,q_a} - \frac{q_a}{2k}\\[2ex] \operatorname{Cos}\theta_{a\underline{k}}\ (iv) &= -\frac{m^{*}\,w_{\underline{q}_o}}{\hbar\,k\,q_a} + \frac{q_a}{2k}\end{aligned}\right) \qquad (3.63)$$

In order to eliminate the δ-functions from (3.58) we note the δ-function property, namely,

$$\delta(ax) = \frac{1}{a}\,\delta(x) \qquad (3.64)$$

Further, we simplify the terms in the square brackets in (3.58). For example, let us consider the first square bracket, namely

$$(1-n_{\underline{k}})(n_{\underline{k}+\underline{q}_o+\underline{q}_a}\ (N_{\underline{q}_o}+1)(N_{\underline{q}_a}+1) - n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_o+\underline{q}_a})N_{\underline{q}_o}\ N_{\underline{q}_a} \qquad ....(3.65)$$

We put

$$n_{\underline{k}} = n^{o}_{\underline{k}} + \frac{\hbar}{m^{*}}\ k_x \chi_{\underline{k}} \qquad (3.66)$$

and

$$n_{\underline{k}+\underline{q}_o+\underline{q}_a} = n^{o}_{\underline{k}+\underline{q}_o+\underline{q}_a} + \frac{\hbar}{m^{*}}\ (\underline{k}+\underline{q}_o+\underline{q}_a)_x\,\chi_{\underline{k}+\underline{q}_o+\underline{q}_a}$$

In the high temperature region one can safely assume that

$$\left.\begin{aligned} (N_{\underline{q}_o} + 1) &\sim N_{\underline{q}_o} = \overline{N}_{\underline{q}_o} \\ (N_{\underline{q}_a} + 1) &\sim N_{\underline{q}_a} = \overline{N}_{\underline{q}_a} \end{aligned}\right\} \qquad (3.67)$$

Here $\overline{N}_{q_o}$ and $\overline{N}_{q_a}$ denote the optical and acoustic phonon equilibrium distribution functions, respectively. In writing the above expression, we have assumed that the phonon distribution function does not change appreciably owing to the scattering process considered here. Thus (3.65) becomes

$$(k_x+q_{ax})\,\chi_{\underline{k}+\underline{q}_o+\underline{q}_a} - k_x\,\chi_{\underline{k}} \qquad \frac{\hbar}{m^*}\,\overline{N}_{\underline{q}_o}\,\overline{N}_{\underline{q}_a} \qquad (3.68a)$$

Similarly, the simplified expressions for other three square brackets can be written respectively, as

$$(k_x-q_{ax})\,\chi_{\underline{k}-\underline{q}_o-\underline{q}_a} - k_x\,\chi_{\underline{k}} \qquad \frac{\hbar\,\overline{N}_{\underline{q}_o}\,\overline{N}_{\underline{q}_a}}{m^*} \qquad (3.68b)$$

$$(k_x+q_{ax})\,\chi_{\underline{k}-\underline{q}_o+\underline{q}_a} - k_x\,\chi_{\underline{k}} \qquad \frac{\hbar\,\overline{N}_{q_o}\,\overline{N}_{q_a}}{m^*} \qquad (3.68c)$$

$$(k_x-q_{ax})\,\chi_{\underline{k}+\underline{q}_o-\underline{q}_1} - k_x\,\chi_{\underline{k}} \qquad \frac{\hbar\,\overline{N}_{\underline{q}_o}\,\overline{N}_{\underline{q}_a}}{m^*} \qquad (3.68d)$$

After substituting (3.59) in (3.58) and integrating over $\theta_{a\underline{k}}$, and using the approximations and simplified forms for the various terms given above we get,

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{net}} = \frac{2\pi}{\hbar}\frac{V}{8\pi^3}\frac{m^*}{\hbar^2 k}\frac{\hbar}{m^*}\sum_{\underline{q}_o}\bar{N}_{\underline{q}_o}\int \bar{N}_{\underline{q}_a}\left|P^{o}_{tt'}\, A^{a}_{t't}\right|^2$$

$$\Big[(k_x+q_{ax})\chi_{\underline{k}+\underline{q}_o+\underline{q}_a} - k_x\chi_{\underline{k}} + (k_x-q_{ax})\chi_{k-q_o-q_a} - k_x\chi_{\underline{k}}$$

$$+(k_x+q_{ax})\chi_{\underline{k}-\underline{q}_o+\underline{q}_a} - k_x\chi_{\underline{k}} + (k_x-q_{ax})\chi_{\underline{k}+\underline{q}_o-\underline{q}_a} - k_x\chi_{\underline{k}}\Big]\, q_a\, dq_a\, d\phi_{ak} \qquad \ldots\ldots\ldots\ldots(3.69)$$

For integration over $d\phi_{a\underline{k}}$, we note the relations[64]

$$q_{ax} = q_a \operatorname{Cos}\theta_{ax} \qquad (3.70)$$

$$k_x = k \operatorname{Cos}\theta_{\underline{k}s} \qquad (3.71)$$

and

$$\operatorname{Cos}\theta_{ax} = \operatorname{Cos}\theta_{a\underline{k}}\operatorname{Cos}\theta_{\underline{k}x} + \operatorname{Sin}\theta_{a\underline{k}}\operatorname{Sin}\theta_{\underline{k}x}\operatorname{Cos}\phi_{a\underline{k}} \qquad \ldots\ldots(3.72)$$

Using (3.62) and (3.72) we get for q_{ax} in the first square bracket of (3.69)

$$q_{ax} = \left[\frac{m^*}{\hbar k^2} w_{\underline{q}_o} - \frac{q_a^2}{2k^2}\right] k_x + q_a \operatorname{Sin}\theta_{a\underline{k}}\operatorname{Sin}\theta_{ax}\operatorname{Cos}\phi_{a\underline{k}} \qquad \ldots\ldots(3.73)$$

Similar expressions for q_{ax} can be written with an appropriate form of $\operatorname{Cos}\theta_{a\underline{k}}$ given by (3.63). We further note that in the integration over $\phi_{a\underline{k}}$, the terms involving Cos $\phi_{a\underline{k}}$ in (3.72) vanish. Also, those terms occurring with $m^* w_{q_o}/\hbar k^2$ will not be important as in the final analysis they will occur in the form multiplied by factors such as

$$\frac{\partial \chi_{\underline{k}}}{\partial E_{\underline{k}}} = \chi^1_{\underline{k}} \tag{3.74}$$

Such terms will be small. This seems to be justified further if we consider the ratio

$$\frac{m^* w_{\underline{q}_o}}{\hbar k^2} = \frac{\hbar w_{q_o}}{\hbar k^2/m^*} \simeq \frac{\hbar w_{q_o}}{2 k_B T} \simeq \frac{2}{15} \tag{3.75}$$

Thus within the above approximations the integration $\phi_{a\underline{k}}$ yields,

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{4\pi^2 V}{\hbar\, 8\pi^3} \frac{m^*}{\hbar^2 K} \frac{\hbar}{m^*} \sum_{q_o} \int_0^{2k} \left| P^o_{tt''} A^a_{t't} \right|^2 q_a dq_a k_x$$

$$= \left[\bar{N}_{\underline{q}_o} \bar{N}_{\underline{q}_a} \left\{ (1 - \frac{q_a^2}{2k^2})(\chi_{\underline{k}+\underline{q}_o+\underline{q}_a} + \chi_{\underline{k}-\underline{q}_o-\underline{q}_a} + \chi_{\underline{k}-\underline{q}_o+\underline{q}_a} + \chi_{\underline{k}+\underline{q}_o-\underline{q}_a}) - 4\chi_{\underline{k}} \right\} \right]$$

.....(3.76)

We now expand terms like $\chi_{k+\underline{q}_o+\underline{q}_a}$ in Taylor's series namely

$$\chi_{\underline{k}+\underline{q}_o+\underline{q}_a} = \chi(E_{\underline{k}} + \hbar\, (w_{\underline{q}_o} + w_{\underline{q}_a})$$

$$= \chi(E_{\underline{k}}) + \hbar\, (w_{\underline{q}_o} + w_{\underline{q}_a})\, \chi'_{\underline{k}} + \ldots \tag{3.77}$$

Making use of the expansions like (3.77), we can write (3.76) in the form

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{-V}{\pi\hbar^4}\ \frac{k_x \chi_{\underline{k}}}{k^3\ c}\ \frac{(k_B T)^2}{W_{q_o}} \sum_{q_o} \int_0^{2k} \left|P^0_{tt'} A^a_{t't}\right|^2 q_a^2 dq_a$$

......(3.78)

In writing down the above expression, we have used the high temperature approximation

$$\bar{N}_{q_o} = \frac{k_B T}{h\ w_{q_a}} \quad \text{and} \quad \bar{N}_{q_o} = \frac{k_B T}{h\ w_{q_o}} \tag{3.79}$$

In order to integrate over q_a, we should know the specific form of $\left|P^o_{tt'} A^a_{t't}\right|^2$. We first assume that the symmetry of the bands is such that the potential due to polarization as well as the dilation waves can connect these two bands. Thus, on the continuum model, we can write for

$$\left|P^o_{tt'} A^a_{t't}\right|^2 = \frac{6\pi^2 e^2 \hbar^2}{4\gamma\ w_{q_o} \rho V^2}\ \frac{\varepsilon_d^2\ q_a^2}{w_{q_a} \Delta E^2_{tt'}\ q_o^2} \tag{3.80}$$

We now substitute (3.80) in (3.78) changing summation over q_o to integration and integrating over q_o and q_a, we get

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = -\ \frac{8\gamma 2\ q_o^{max}\ (k_B T)^{5/2} (m^*)^{3/2}\ e^2\ {}^2_d}{h^4\ c^2\ w^2_{q_o} \gamma \rho \pi\ \Delta E^2_{tt'}}\ \frac{h\ k_x}{m^*}\quad \underline{k}$$

... (3.81)

where q_o^{max} is the upper limit of q_o. Comparing (3.81) with the relation (3.57)

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = - \frac{\hbar k_x}{m^* \tau} \chi_{\underline{k}} \qquad (3.82)$$

we get

$$\frac{1}{\tau} = \frac{8\sqrt{2}\,(k_B T)^{5/2}\,(m^*)^{3/2}\,q_o^{max}\,e^2\,\mathcal{E}_d^2}{\hbar^4\,c^2\,w_{q_o}^2\,r\,\rho\,\pi\,\Delta E_{tt'}^2} \qquad (3.83)$$

Hence

$$\mu = \frac{e\tau}{m^*} = \mu_o^{(o)}\,T^{-5/2}\,, \qquad (3.84)$$

where

$$\mu_o^{(o)} = \frac{\pi\,\hbar^4\,c^2\,w_{\underline{q}_o}^2\,r\,\rho\,\Delta E_{tt'}^2}{8\sqrt{2}\;e\;\mathcal{E}_d^2\,(m^*)^{5/2}\,q_o^{max}\,k_B^{5/2}} \qquad (3.85)$$

Next we consider the interaction terms given by (3.35). The first term (3.35a) describes the one phonon process involving optical phonons. Such processes are not considered in the present investigation as they have been dealt with elsewhere.[5] The terms given by (3.35b) and (3.35c) describe the two-phonon processes as remarked in the earlier section. Here both the phonons are optical phonons and we consider only these terms in the present calculation. However, from these terms we omit those involving the simultaneous creation or annihilation of $b^*_{\underline{q}_o}\,b^*_{\underline{q}_o}$, $b_{\underline{q}_o}\,b_{\underline{q}_o}$, etc. as they will not conserve energy.

Now, we restrict our attention to the terms such as

$$H^{(1)}_{int}\ (0-0) = \sum_{t',\underline{q}_o,\underline{q}'_o} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}'_o} \middle| U_{\underline{k}'t} \right\rangle \left\langle U_{\underline{k}'t} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}t} \right\rangle$$

$$\times \left[a^{*}_{\underline{k}+\underline{q}_o-q'_o}\, a_{\underline{k}} b_{\underline{q}_o} b^{*}_{\underline{q}'_o} - a_{\underline{k}+\underline{q}_o-\underline{q}'_o} a^{*}_{\underline{k}_o} b^{*}_{\underline{q}_o} b_{\underline{q}'_o} \right] \frac{1}{\Delta E_{tt'}},$$

..........(3.86)

and

$$H^{(2)}_{int}\ (0-0) = \sum_{t'\underline{q}_o\underline{q}'_o} \left\langle U_{\underline{k}''t} \middle| P_{\underline{q}'_o} \middle| U_{\underline{k}'t'} \right\rangle \left\langle U_{\underline{k}'t'} \middle| P_{\underline{q}_o} \middle| U_{\underline{k}t} \right\rangle$$

$$\times \left[a^{*}_{\underline{k}-\underline{q}_o+\underline{q}'_o}\, a_{\underline{k}} b^{*}_{\underline{q}_o} b_{\underline{q}'_o} - a_{\underline{k}-\underline{q}_o-\underline{q}'_o} a^{*}_{\underline{k}} b_{\underline{q}}\ b^{*}_{\underline{q}'} \right] \frac{1}{\Delta E_{tt'}},$$

..........(3.87)

The rate of change of the distribution function of the charge carriers $(\partial n_{\underline{k}} / \partial t)_{net}$ due to the interaction processes given by (3.86) and (3.87) is written as

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{2\pi}{\hbar} \sum_{\underline{q}_o,\underline{q}'_o} \left| P'_{tt'}\ \ P_{t't} \right|^2$$

$$\times \Big\{ \Big[(1-n_{\underline{k}})(n_{\underline{k}+\underline{q}_o-\underline{q}'_o})(N_{\underline{q}_o}+1)(N_{\underline{q}'_o}) - n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_o-\underline{q}'_o})(N_{\underline{q}_o})(N_{\underline{q}'_o}+1) \Big]$$

$$\times\ \delta(E_{\underline{k}+\underline{q}_o-\underline{q}'_o} - E_{\underline{k}} + \hbar(w_{\underline{q}_o} - w_{\underline{q}'_o}))$$

$$+ \Big[(1-n_{\underline{k}})(n_{\underline{k}-1_o+\underline{q}'_o})(N_{\underline{q}_o})(N_{\underline{q}'_o}+1) - n_{\underline{k}}(1-n_{\underline{k}-\underline{q}_o+\underline{q}'_o})(N_{\underline{q}_o}+1)(N_{\underline{q}'_o}) \Big]$$

$$\times\ \delta(E_{\underline{k}-\underline{q}_o+\underline{q}'_o} - E_{\underline{k}} - \hbar(w_{\underline{q}_o} - w_{\underline{q}'_o})) \Big\}$$

.......(3.38)

In simplifying the expression (3.88) further, we change the summation over q_o to integration. For convenience, we express the volume element appearing in the integration in polar coordinates $(q_o, \theta_{ok}, \phi_{ok})$. The wave vector q_o' of one of the optical phonon is restricted to a small range from 0 to q_o^{max}. Further we take q_o' along the polar axis. For optical modes, it is customary to take the same frequency for all the modes i.e. $\hbar w_{\underline{q}_o} = \hbar w_{\underline{q}_o'}$. It follows from this that $\bar{N}_{\underline{q}_o'} = \bar{N}_{\underline{q}_o} = \bar{N}_{\underline{q}_o}$ and in the high temperature region we use,

$$\bar{N}_{\underline{q}_o} = \frac{k_B T}{\hbar w_{\underline{q}_o}} = (\overline{N_{\underline{q}_o}+1}). \tag{3.89}$$

With these assumptions and approximations in view, we simplify the various terms occurring in (3.88). Let us consider the square bracket terms first. As done in the acoustic phonon scattering case, we can write

$$(1-n_{\underline{k}})(n_{\underline{k}+\underline{q}\ -\underline{q}'})(N_{\underline{q}_o}+1)(N_{\underline{q}_o'})-n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_o-\underline{q}_o'})N_{\underline{q}_o}(N_{\underline{q}_o'}+1)$$

$$= \frac{\hbar}{m^*}\bar{N}_{\underline{q}_o'}\bar{N}_{\underline{q}_o}\left[(k_x+q_{ox})\chi_{\underline{k}+\underline{q}_o-\underline{q}_o'} - k_x\chi_k\right] \tag{3.90}$$

and

$$(1-n_{\underline{k}})(n_{\underline{k}-\underline{q}_o+\underline{q}_o'})(N_{\underline{q}_o})(N_{\underline{q}_o'}+1) - n_{\underline{k}}(1-n_{\underline{k}-\underline{q}_o+\underline{q}_o'})(N_{\underline{q}_o}+1)(N_{\underline{q}_o'})$$

$$= \frac{\hbar}{m^*}\bar{N}_{\underline{q}_o'}\bar{N}_{\underline{q}_o}\left[(k_x-q_{ox})\chi_{\underline{k}-\underline{q}_o+\underline{q}_o'} - k_x\chi_k\right] \tag{3.91}$$

We can simplify the δ-functions under the above assumptions as

$$\delta(E_{\underline{k}+\underline{q}_0-\underline{q}'_0} - E_{\underline{k}} + \hbar\,(w_{\underline{q}_0} - w_{\underline{q}_0})$$

$$= \delta(E_{\underline{k}+\underline{q}_0-\underline{q}'_0}-E_{\underline{k}})\;\delta\,(\frac{\hbar^2 k q_0}{m^*}\left[\frac{q_0}{2k} + \cos\theta_{ko}\right]\;\frac{m^*}{\hbar^2 k q_0}\,\delta(\cos\theta_{ko}+\frac{q_0}{2k})$$

.... (3.92)

and

$$\delta\,(E_{k-\underline{q}_0+\underline{q}'_0} - E_{\underline{k}} - \hbar\,(w_{\underline{q}_0} - w_{\underline{q}'_0})$$

$$= \delta(E_{\underline{k}-\underline{q}_0+\underline{q}'_0} - E_{\underline{k}})\;\frac{m^*}{h^2 k q_0}\;\delta\,(-\cos\theta_{ko} + \frac{q_0}{2k}) \quad \ldots (3.93)$$

Substituting (3.90) to (3.93) in (3.88) and integrating over θ_{ok} and ϕ_{ok} we get

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{-V\;k_x\varkappa_k}{2\pi\;h^2\;k^3}\sum_{\underline{q}'_0}\int_0^{2k}\left|P'_{tt'}\,P_{t't}\right|^2\,\bar{N}_{\underline{q}'_0}\,\bar{N}_{\underline{q}_0}\,q_0^3\,dq_0$$

... (3.94)

In order to write down the specific form of $|P'_{tt'}\,P_{t't}|$ appearing in (3.94) we follow the method of deformation potential for optical modes developed by Seitz.[31] Thus we can write down[5] $P_{tt'} \propto \frac{g_3}{E_{tt'}}$. This is obvious from matrix element (1.27) .

Thus

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = - \frac{\hbar k_x \chi_k}{m^*} \frac{\sqrt{2}\, \varepsilon_3^4\, g^4 (k_B T)^{5/2} (q_0^{max})^3 (m^*)^{5/2}}{12\, \hbar^4\, \rho^2\, w_{q_0}^4\, \Delta E_{tt'}^2\, \pi^3} \qquad ..(3.95)$$

and

$$\frac{1}{\tau} = \frac{\sqrt{2}\, \varepsilon_3^4\, g^4 (k_B T)^{5/2} (q_0^{max})^3\, (m^*)^{3/2}}{12\, h^4\, \rho^2\, w_{q_0}^4\, \Delta E_{tt'}^2\, \pi^3} \qquad ..(3.96)$$

It is seen that the above also gives

$$\mu = \mu_0^{(o)}\, T^{-5/2} \qquad (3.97)$$

with

$$\mu_0^{(o)} = \frac{12\, \hbar^4\, \rho^2\, w_{q_0}^4 \Delta E_{tt'}^2\, \pi^3\, e}{\sqrt{2}\, \varepsilon_3^4\, g^4 (k_B T)^{5/2} (q_0^{max})^3\, (m^*)^{5/2}} \qquad (3.98)$$

Atomistic model

In the preceding calculations of relaxation time and mobility we have considered a continuum model for the interaction processes. In what follows, we consider the interaction processes on the atomistic model. In this description the perturbing potential can be considered in terms of the oscillating crystal field which the carrier at a site n will experience owing to the motion of its neighbouring ions. The interaction terms are similar to one given in (3.35) except for the following differences.

1) In deriving the interaction term for the present case, we construct the Bloch's solution of the unperturbed problem with the help of atomic like functions namely, U_{nt}. Thus, we get the Bloch's function of the form

$$\phi_{kt} = \frac{1}{\sqrt{V}} \sum_{n} U_{nt} \, e^{i \, \underline{k}\cdot\underline{R}_n} \qquad (3.99)$$

2) The expression

$$\left| P'_{tt'} \, P_{t't} \right| = \left| \frac{\langle U_{\underline{k}''t} | P_{\underline{q}_0'} | U_{\underline{k}'t'} \rangle \langle U_{\underline{k}'t'} | P_{\underline{q}_0} | U_{\underline{k}t} \rangle}{\Delta E_{tt'}} \right|^2$$

is now replaced by

$$\left| \frac{\langle U_{nt} | P_{\underline{q}_0'} | U_{nt'} \rangle \langle U_{nt'} | P_{\underline{q}_0} | U_{nt} \rangle}{\Delta E_{tt'}} \right|^2 \qquad (3.100)$$

3) In obtaining (2) we have used the form given by (3.8) for optical modes so that we can write down

$$\left| \frac{\langle U_{nt} | P_{\underline{q}_0'} | U_{nt'} \rangle \langle U_{nt'} | P_{\underline{q}_0} | U_{nt} \rangle}{\Delta E_{tt'}} \right|^2$$

$$= \left| \frac{\langle U_{nt} | g_{\underline{q}_0'} \, F(r,\underline{R}_n) | U_{nt'} \rangle \langle U_{nt'} | g_{\underline{q}_0} \, F(r,\underline{R}_n) | U_{nt} \rangle}{E_{tt'}} \right|^2$$

$$\frac{g^2_{\underline{q}_0'} \, g^2_{\underline{q}_0}}{\Delta E^2_{tt'}} \left| F_{tt'} \, F_{t't} \right|^2 \qquad \ldots (3.101)$$

Thus the two phonon interaction terms can be written with these changes, as

$$H_{int}(0\text{-}0) = 4 \sum_{t'} F_{tt'}\, F_{t't}\, g_{\underline{q}_0}\, g_{\underline{q}_0'}$$

$$\Big[a^*_{\underline{k}-\underline{q}_0'-\underline{q}_0}\, a_{\underline{k}} b^*_{\underline{q}_0} b^*_{\underline{q}_0} - a^*_{\underline{k}-\underline{q}_0'+\underline{q}_0}\, a_{\underline{k}} b^*_{\underline{q}_0'} b_{\underline{q}_0}$$

$$- a^*_{\underline{k}-\underline{q}_0'-\underline{q}_0}\, a_{\underline{k}} b'_{\underline{q}} b^*_{\underline{q}_0} + a^*_{\underline{k}+\underline{q}_0'+\underline{q}_0}\, a_{\underline{k}} b_{\underline{q}_0'} b_{\underline{q}_0} + \text{c.c.} \Big]$$

..........(3.102)

In accordance with the remarks made earlier, we disregard those terms which involve the simultaneous creation and annihilation of two phonons. Therefore we have to consider only second and third terms and their c.c. terms in (3.102).

Repeating the earlier calculations for the interaction terms in (3.102) under consideration, we get

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = - \frac{8 k_x \underline{k}\, V\, \overline{N}_{\underline{q}_0} \overline{N}_{\underline{q}_0'}}{\hbar^2 \pi k^3 \triangle E^2_{tt'}}\, g^2_{\underline{q}_0} g^2_{\underline{q}_0'} \sum_{q_0'} \int_0^{2k} \left| F_{tt'}\, F_{t't} \right|^2 q_0^3\, dq$$

.... (3.103)

$$= - \frac{4\, \overline{N}_{\underline{q}_0} \overline{N}_{\underline{q}_0'}\, k\, (q_0^{max})^3\, \hbar\, k_x \chi_k}{3 \pi^3 \rho^2\, w^2_{\underline{q}_0} \triangle E^2_{tt'}\, m^*} \left| F_{tt'}\, F_{t't} \right|^2 \frac{m^*}{\hbar}$$

.... (3.104)

Finally we get $\mu = \mu_o^{(o)} \, T^{-5/2}$ (3.105)

where

$$\mu_o^{(o)} = \frac{3 \hbar^4 \, e \, \pi^3 \, W^2_{\underline{q}_o} \, \Delta E^2_{tt'} \, \rho^2}{4\sqrt{2} \, (q_o^{max})^3 \, (m^*)^{5/2} \, |F_{tt'} \, F_{t't}|^2} \qquad (3.106)$$

PbS group solid solutions[60]

We shall now obtain the relevant relaxation time and the mobility expressions for the solid solution of the PbS group semiconductors. We proceed in the same manner as in the preceding case, namely, the pure PbS group. Here also we restrict our attention to a two band model for the system under consideration. Further the third order term in the interaction Hamiltonian (3.51) is expected to be unimportant compared to the first and second order terms. Hence, neglecting the third order term in (3.51) we can write down the interaction Hamiltonian as

$$H_{int} = \sum_{\underline{q}_a} \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{kt}} \right\rangle + \frac{V^{(p)}_{\underline{k}''t,\underline{k}'''t''} \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{kt}} \right\rangle}{\Delta E_{tt''}}$$

$$+ \left\langle U_{\underline{kt}} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}'t'} \right\rangle \frac{V^{(p)}_{\underline{k}'t';\underline{k}t}}{\Delta E_{tt'}} \qquad (3.107)$$

Thus, we get for the rate of change of distribution function of the charge carriers owing to the processes given by (3.107)

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{\text{net}} = - \frac{n_{\underline{k}} - n_{\underline{k}}^{o}}{\tau}$$

$$= \frac{2\pi}{\hbar} \sum_{\underline{q}_a} \left\{ 4 \left| V^{(p)}_{\underline{k}''t;\underline{k}'''t''} \left\langle U_{\underline{k}'''t''} \right| A_{\underline{q}_a} \left| U_{\underline{k}t} \right\rangle \right|^2 + \left| \left\langle U_{\underline{k}''t} \right| A_{\underline{q}_a} \left| U_{\underline{k}t} \right\rangle \right|^2 \right\}$$

$$\times \left\{ \left[(1-n_{\underline{k}})n_{\underline{k}-\underline{q}_a} N_{\underline{q}_a} - n_{\underline{k}}(1-n_{\underline{k}-\underline{q}_a})(N_{\underline{q}_a}+1) \right] \delta(E_{\underline{k}-\underline{q}_a} - E_{\underline{k}} + \hbar W_{\underline{q}_a}) + \left[(1-n_{\underline{k}})n_{\underline{k}+\underline{q}_a}(N_{\underline{q}_a}+1) - n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_a})N_{\underline{q}_a} \right] \delta(E_{\underline{k}+\underline{q}_a} - E_{\underline{k}} - \hbar W_{\underline{q}_a}) \right\}$$

.... (3.108)

In writing down (3.108) we have considered the contribution of second and third terms of (3.107) as the same; hence the appearance of factor 4. In order to obtain the explicit form of the terms included in the first curly bracket, we assume a random distribution[4,26] of the solute atoms of the solid solution. Further we note that $\sum_{s} f_s = 1$, where s is the type of atom in the solid solution.

Thus we have

$$\left| \frac{V^{(p)}_{\underline{k}''t,\underline{k}'''t''}}{\Delta E_{tt''}} \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \right|^2$$

$$= \sum_{r,s} \frac{f_r f_s}{2} \left| \left\langle U_{\underline{k}''t} \middle| V_r - V_s \middle| U_{\underline{k}'''t''} \right\rangle \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle \right|^2 \qquad \ldots\ldots\ (3.109)$$

For convenience in notation we write

$$F_{rs} = \left\langle U_{\underline{k}''t} \middle| V_r - V_s \middle| U_{\underline{k}'''t''} \right\rangle \qquad (3.110)$$

Here V_r and V_s are atomic like potentials of the atoms r and s respectively.

Further, using the relation (3.13b) we can write

$$\left.\begin{aligned} \left\langle U_{\underline{k}'''t''} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle^2 &= \frac{\hbar\, q_a^2\, \varepsilon_{d'}^2}{2 \rho\, w_{\underline{q}_a} V} \\ \left\langle U_{\underline{k}''t} \middle| A_{\underline{q}_a} \middle| U_{\underline{k}t} \right\rangle^2 &= \frac{\hbar\, q_a^2\, \varepsilon_{d_{1,2}}^2}{2 \rho\, w_{\underline{q}_a} V} \end{aligned}\right\} \qquad (3.111)$$

Here $\varepsilon_{d'}$ refers to the deformation potential for scattering by acoustic mode involving inter-band transitions and $\varepsilon_{d_{1,2}}$ denotes the deformation potential for the pure phase 1 or 2. For example, the suffix 1 may stand for PbTe and 2 for PbSe.

Substituting (3.109), (3.110) and (3.111) in (3.108) and changing the summation over $\underline{q}_a$ to the corresponding integration we get,

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{2\pi}{\hbar}\,\frac{V}{8\pi^3}\int dq_a \left\{ \frac{4\sum_{r,s} f_r f_s\,|F_{rs}|^2\,\hbar\varepsilon^2_{d'}}{4\,\Delta E^2_{tt''}\,\rho V} + \frac{\hbar\varepsilon^2_{d_{1,2}}}{2\rho V} \right\}$$

$$\times \left(\frac{q_a^4}{w_{\underline{q}_a}}\,\sin\theta_{a\underline{k}}\;d\theta_{ak}\;d\phi_{a\underline{k}}\right)$$

$$\times \left\{ \left[(1-n_{\underline{k}})\,n_{\underline{k}-\underline{q}_a}\,N_{\underline{q}_a} - n_k(1-n_{\underline{k}-\underline{q}_a})(N_{\underline{q}_a}+1)\right] \right.$$

$$\times\ \delta(E_{\underline{k}-\underline{q}_a} - E_{\underline{k}} - \hbar w_{\underline{q}_a})$$

$$+ \left[(1-n_{\underline{k}})\,n_{\underline{k}+\underline{q}_a}\,(N_{\underline{q}_a}+1) - n_k(1-n_{\underline{k}+\underline{q}_a})\,N_{\underline{q}_a}\right]$$

$$\left. \times\ \delta(E_{\underline{k}+\underline{q}_a} - E_k + \hbar w_{\underline{q}_a}) \right\} \qquad \ldots(3.112)$$

Following the method adopted in simplifying (3.65) we get for the square bracket terms in (3.112),

$$(1-n_{\underline{k}})\,n_{\underline{k}-\underline{q}_a}\,N_{\underline{q}_a} - n_{\underline{k}}(1-n_{\underline{k}-\underline{q}_a})(N_{\underline{q}_a}+1)$$

$$= \frac{\hbar N_{\underline{q}_a}}{m^*}\left[\chi_{\underline{k}-\underline{q}}\,(k_x - q_{ax}) - \chi_{\underline{k}}\,k_x\right]$$

and

$$(1-n_{\underline{k}})n_{\underline{k}+\underline{q}_a}\ (N_{\underline{q}_a}+1) - n_{\underline{k}}(1-n_{\underline{k}+\underline{q}_a})N_{\underline{q}_a}$$

$$\frac{\hbar\,\overline{N}_{\underline{q}_a}}{m^*}\ \chi_{\underline{k}+\underline{q}_a}\ (\,K_x + q_{ax}) - \chi_k\,K_x \qquad ..\ (3.113)$$

The arguments of the δ-function can be written as

$$E_{\underline{k}\,\mp\,\underline{q}_a} - E_k \pm \hbar\, w_{\underline{q}_a} = \frac{\hbar^2 k q_a}{m^*}\Big(\ \frac{q_a}{2k} \mp \cos\theta_{a\underline{k}} \pm \frac{m^*\, w_{\underline{q}_a}}{\hbar\, k q_a}$$

$$\ldots\ldots\ (3.114)$$

Substituting (3.113), (3.114) in (3.112) and integrating over $\theta_{a\underline{k}}$ (for the elimination of δ-function) and $\phi_{a\underline{k}}$ we get,

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \left(\frac{2\,\xi^2_{d'}\ \overline{\sum_{r,s}}\ f_{r'}\, f_s\ |P_{rs}|^2}{\Delta E^2_{tt''}} + \xi^2_{d_{1,2}}\right)\frac{K_x\chi_k(k_BT)}{4\pi\ \hbar^2\ k\ c^2}$$

$$\times\int_0^{2k} q_a\, dq_a\ (\ -\ \frac{q_a^2}{k^2}) \qquad \ldots\ldots\ (3.115)$$

where the following approximations have been made:

$$\overline{N}_{\underline{q}_a} = \frac{k_BT}{\hbar\, w_{\underline{q}_a}}\ ; \qquad w_{\underline{q}} = c\,\underline{q}_a$$

c being the velocity of sound. The final integration over q_a gives us

$$\left(\frac{\partial n_{\underline{k}}}{\partial t}\right)_{net} = \frac{-\hbar k_x k (k_B T)^{3/2} \sqrt{2} (m^*)^{3/2}}{m^* \pi \rho \hbar^4 c^2}$$

$$\times \left(\varepsilon^2_{d_{1,2}} + \frac{2 \varepsilon^2_{d'} \sum_{r,s} f_r f_s |F_{rs}|^2}{\Delta E^2_{tt''}} \right) = - \frac{\hbar k_x \underline{k}}{m^*}$$

............(3.117)

Thus, we get,

$$\frac{1}{\tau} = \frac{\sqrt{2} (k_B T)^{3/2} (m^*)^{3/2}}{\pi \rho c^2 \hbar^4} \left(\varepsilon^2_{d_{1,2}} \frac{2 \varepsilon^2_{d'} \sum_{r,s} f_r f_s |F_{r,s}|^2}{\Delta E^2_{tt''}} \right)$$

.... (3.118)

The mobility expression μ can be written as

$$\mu = \frac{e \tau}{m^*} = \mu_o^{(s)} T^{-3/2} \qquad (3.119)$$

where

$$\mu_o^{(s)} = \frac{e \pi \rho c^2 \hbar^4}{\sqrt{2} (k_B)^{3/2} (m^*)^{5/2} \left(\varepsilon^2_{d_{1,2}} + \frac{2 \varepsilon^2_{d'} \sum_{r,s} f_r f_s |F_{rs}|^2}{\Delta E^2_{tt''}} \right)}$$

......(3.120)

It follows from (3.120) that when one or the other component in the solid solution is zero, the expression $\mu_o^{(s)}$ reduces to

$$\mu_o^{(s)} \quad (\text{pure}) = \frac{e \quad \pi \rho c^2 \hbar^4}{(k_B)^{3/2} \sqrt{2} \; (m^*)^{5/2} \; \varepsilon^2_{d_{1,2}}} \tag{3.121}$$

In deriving the expression (3.120) we have assumed that the effective mass of the charge carriers m^* remains unchanged. This is approximately true. Next, we consider the alloy concentration dependence of band gap $\Delta E_{tt''}$. The band gap is known to depend on the alloy concentration and can be inferred from the theoretical work of Parmenter on Ge-Si alloys.[05] Thus, we assume the form

$$\Delta E_{tt''} = f_r \, \Delta E_{tt''}^{(r)} + f_s \, \Delta E_{tt''}^{(s)} \tag{3.122}$$

Here $\Delta E_{tt''}^{(r)}$ is the gap for the pure phase r (say PbTe) and $\Delta E_{tt''}^{(s)}$ for the other component when pure. Further, we note that the form given in (3.122) reproduces the experimental dependence on the alloy concentration for the system PbTe-PbSe as observed by Scanlon.[46]

It is helpful for later discussion to write down the combined result of the previous section with the present result. Thus, we can write down the sum total of the mobility,

$$\frac{1}{\mu_T} = \frac{1}{\mu_o^{(s)} T^{-3/2}} + \frac{1}{\mu_o^{(o)} \; T^{-5/2}} \tag{3.123}$$

CHAPTER - 4

A. DISCUSSION AND ESTIMATES.

In the foregoing chapter, we have developed a theory of carrier mobility both for PbS group and their solid solutions. We shall now discuss the various models adopted in the calculation and estimate the magnitude of the mobility in a typical case. For this purpose, we shall consider the two cases separately.

(1) PbS group

The theory developed in the preceding chapter shows that the two phonon processes, one acoustical and other optical as well as both optical give rise to expressions for mobility of charge carriers having the right kind of temperature dependence i.e.

$$\mu = \mu_o^{(o)} T^{-5/2} \tag{4.1}$$

We note that both the continuum model and atomistic model lead to the same temperature dependence of mobility, although the temperature independent part is slightly different.

First, let us consider the expressions (3.84) and (3.97) derived under the assumption of the continuum model. In obtaining these expressions, we have assumed that one of the optical phonons assists the inter-band transitions. This is because of the fact that the full band and empty band are both admixtures of s and p bands in lead chalcogenides. Thus the matrix elements connecting the two bands seem to be non zero for the situations considered above.

Now we shall consider some estimates of the expression (3.84) for the semiconductor PbS. We utilize the following values of the parameters as given by Scanlon.[41]

$$\epsilon_o = 17.9 \qquad \epsilon_\infty = 15.3 \qquad \rho = 7.5$$

$$\Delta E_{tt'} = 0.37 \text{ ev.} \qquad m^* = m_e \, (0.17)$$

where m_e is the free electron mass.

From (1.29) we have

$$\gamma w^2_{\underline{q}_o} = \frac{4\pi \epsilon_o \epsilon_\infty}{\epsilon_o - \epsilon_\infty} \quad , \qquad c = 5 \times 10^5 \text{ cm/sec.}$$

Let us take the deformation potential $\mathcal{E}_d = 1$ eV. Using the above values we get μ at room temperature of the order 10^2 cm^2 / volt-sec. The observed value quoted by Scanlon[41] for PbS, PbSe and PbTe is in the range 10^2 to 10^3 cm^2/volt-sec. For more accurate estimate, we should insert the precise figures for the band gap, the deformation potential and the effective mass. In fact, some recent optical measurements on PbS suggest the values[66]

$$\epsilon_o = 140 \quad (\text{ R. Geick })$$

$$\epsilon_o = 174 \quad (\text{ Z. Zemel })$$

On using these values, one can expect a slight modification in the estimation of μ.

However, we have taken $q_o^{max} = 10^6 \text{ cm}^{-1}$ in the estimation of the mobility, but it is more appropriate to use a smaller value of q_o^{max}. Thus one would expect an order of magnitude agreement between experiment and theory.

Now we consider the expression (3.97). In obtaining this expression, we have assumed both the phonons participating in the scattering processes as optical phonons. An estimate of this expression is difficult in the sense that we do not have any knowledge of parameters ε_3 and g occurring in the expression. Hence we do not estimate this expression and leave this at this stage.

Let us consider the mobility expression (3.105). In order to obtain this we have utilized an atomistic model. For the interaction mechanism we have considered the two phonon processes, wherein both the phonons are of optical type. The value of the propagation vector of one of the phonon is taken to be very small. This is done in order to solve approximately the δ-function part of integration which in our case involves energy conservation terms such as

$$E_{\underline{k}} - E_{\underline{k}''} + \hbar (w_{\underline{q}_o} - w_{\underline{q}_o'}) = 0$$

The second reason is that for the "reststrahlen" mode, which interact strongly with the ionic lattice, the propagation vector has a small value. Such modes are particularly important for the interband transitions envisaged in the present work. The inter-band transitions are caused by the perturbing potential owing to the crystal field oscillations around an atom. Such transitions may be likened to an intra-atomic transition say from s state to p state. Such configuration mixing owing to the crystal field oscillation is significant and has an important role in optical and magnetic studies of ionic solids.[67,68,69] Such effects were found to be of importance in NiO type semiconductors.[70]

The perturbing potential noted above can be obtained by a crystal field calculation for a pair of atoms PbX as suggested by Sinha and Sinha[70] and is given by

$$F(r,\underline{R}_h) = \pm \left|Qe^2\right| \left(\frac{1}{R_h^2} + \frac{2z}{R_h^3} + \frac{3}{2}\,\frac{(3z^2-r^2)}{R_h^4} + \ldots. \right)$$

This potential connects the atomic states and the matrix element

$$\left\langle s \,\middle|\, \pm \; Qe^2 \; \frac{2z}{R_h^3} \,\middle|\, p \right\rangle = F_{tt'} \quad \text{is non-zero.}$$

The magnitude of $F_{tt'}$ is of the order of 10^{-4} dynes as suggested by Sinha and Sinha.[70] Assuming $F_{tt'} = 10^{-4}$ dynes, $\triangle E_{tt'} = 0.37$ eV and $\hbar w_{q_0} = 0.008$ eV to 0.02 eV (the corresponding Einstein's temperature of the solid being, 100°K to 200°K), we see that the room temperature mobility value ranges from 10^2 to 10^3 cm^2/volt-sec. Thus the atomistic model gives a fairly satisfactory magnitude of the mobility.

(2) PbS group solid solution

We next analyse the mobility expression obtained in the chapter 3 for the case of solid solutions of PbS group. For the theoretical analysis of the carrier mobility we have invoked inter-band transitions of the charge carriers owing to the perturbations caused by alloying effect. We have shown that the perturbing potential can be obtained by a crystal field calculation (see appendix) for the system under consideration. Further we have assumed that the perturbing potential admixes the atomic states as can be seen from its form. Then we have considered one-phonon (acoustic mode) scattering of the charge carriers with orbital functions modified owing to the change in the crystal potential as a result of alloying. We discuss the situation in the low and high temperature regions. (Here low temperature refers to region $\sim$ 50°K and not in the liquid helium temperature region). In the low temperature region the mobility expression is of the form $\mu = \mu_0^{(s)} T^{-3/2}$. As the temperature is raised the optical modes get populated. Thus in the high temperature region two-phonon processes discussed in the foregoing section will dominate and the mobility expression will be of the form $\mu = \mu_0^{(s)} T^{-5/2}$. These situations can be easily seen from the mobility expression (3.123). In order to have a clear insight into the two forms remarked above let us rewrite the expression (3.123) in the form

$$\mu_T = \frac{\mu_0^{(s)} \, \mu_0^{(o)} \, T^{-5/2}}{\mu_0^{(o)} \, T^{-1} + \mu_0^{(s)}} \qquad (4.2)$$

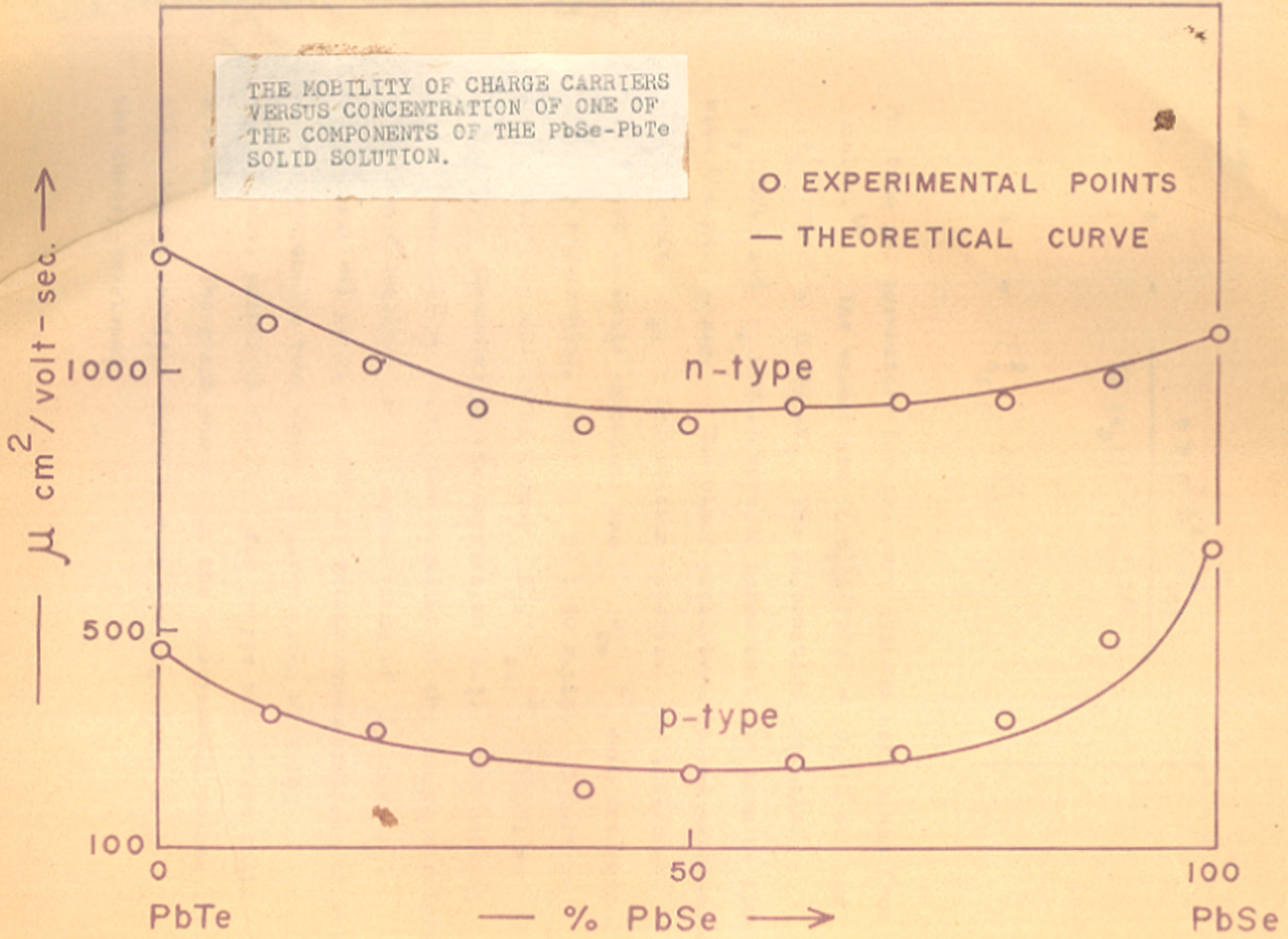
If one sets the condition $\mu_o^{(o)}T^{-1} \gg \mu_o^{(s)}$ in the above one can neglect $\mu_o^{(s)}$ in the denominator of μ_T. Thus one gets, $\mu_T = \mu_o^{(s)}T^{-3/2}$. On the other hand, setting the condition $\mu_o^{(c)}T^{-1} \ll \mu_o^{(s)}$, the mobility expression comes out to be of the form $\mu_T = \mu_o^{(e)}T^{-5/2}$. This is indeed the experimental behaviour.[48] Further, in the solid solution the magnitude of $\mu_o^{(s)}$ goes down owing to the presence of extra term in the denominator of (3.120). Hence the $T^{-5/2}$ behaviour in solid solution should take over at a lower temperature than in the pure case. This is in agreement with the experimental facts.[48]

Let us now analyse the concentration dependence of mobility of charge carriers. We compare the experimental results of solid solution (PbTe-PbSe) given by Joffe and collaborators[48] with the theory as given by (3.119). The two components of the system considered are miscible in all proportions and therefore they constitute a fairly good system for the test of the theory. Further, as remarked earlier we take the form (3.122) for $\Delta E_{tt''}$ in (3.119).

For comparison, we rewrite the mobility expression (3.119) as

$$\mu_o^{(s)} = \frac{e\,\pi\,\rho\,c^2\,\hbar^4\,\Delta E_{tt''}^2}{\sqrt{2}\,(k_B T)^{3/2}(m^*)^{5/2}\left[\xi_{d_{1,2}}^2\,\Delta E_{tt''}^2 + 2\,\xi_d^2 \sum\limits_{r,s} f_r f_s |F_{rs}|^2\right]}$$

$$= \frac{a}{b + 2\,\xi_{d'}^2 \sum\limits_{r,s} f_r f_s\,|F_{rs}|^2} \qquad \ldots.(4.3)$$



THE MOBILITY OF CHARGE CARRIERS VERSUS CONCENTRATION OF ONE OF THE COMPONENTS OF THE PbSe-PbTe SOLID SOLUTION.

where

$$\left.\begin{aligned} a &= \frac{e\,\pi\,c^{2}\,\hbar^{4}\,\Delta E^{2}_{tt''}}{\sqrt{2}\,(k_{B}T)^{3/2}\,(m^{*})^{5/2}} \\ \\ b &= \varepsilon^{2}_{d_{1,2}}\;\Delta E^{2}_{tt''} \end{aligned}\right\} \qquad (4.4)$$

The band gap parameters for the pure systems were taken from Scanlon.[46] The values are $\Delta E^{(r)}_{tt''}$(PbTe) = 0.318 eV and $\Delta E^{(s)}_{tt''}$(PbSe) = 0.283 eV. The deformation potential ε_{d_1}(PbTe) and ε_{d_2}(PbSe) were so taken that the results fitted with the pure cases. The other parameters is the expression which involve $\varepsilon_{d'}$ (deformation potential for interband transition in solid solution) and $|F_{rs}|^{2}$ were determined from the experimental point at 50 : 50 ratio. Infact we have determined the whole factor $\varepsilon^{2}_{d'}$, $|F_{rs}|^{2}$. Thus, we get all the constants in the expression (4.3). Now setting these constants in (4.3), the mobility of the charge carriers have been calculated for different value of f_r and f_s. The theoretical graph of mobility versus concentration of one of the components thus drawn is given along with the experimental points in Fig. (5) for p-type and n-type solid solutions. The graph shows that the experimental points lie all along theoretical curve in very good agreement with the theory developed.

B. CONCLUDING REMARKS

In the foregoing chapters, we have developed a theory of carrier mobility in polar semiconductors and their solid solutions. The concept of inter-band transition of charge carriers caused by optical phonons or alloying perturbation potential was introduced. The modified electronic orbitals were used in the scattering problem.

In the pure case (PbS group) the role of both the acoustic and the optical (or polar-optical) modes for the scattering processes were considered. In such a formulation, we came across processes involving one, two and three phonons. Considering only two phonon processes involving one acoustic and one optical as well as two optical phonons, we obtained the mobility expression of the type $\mu = \mu_0^{(0)} T^{-5/2}$. The $T^{-5/2}$ law obtained theoretically is in very good agreement with the experimentally observed temperature dependence of mobility. For the two-phonon processes (acoustic-optical) in the continuum approximation the room temperature value of the mobility is of the order 10^2 cm^2 / Volt-sec. We found that for the two phonon processes involving both optical modes in the continuum approximation, the estimation of the mobility expression is somewhat difficult in as much as we do not know the values of some of the parameters occurring in the mobility expression.

In the solid solution of PbS group (eg. PbTe-PbSe) the formulation in terms of the perturbed electronic states which incorporates the effect of inter-band mixing owing to the alloy perturbation leads to one phonon process involving acoustic mode. The mobility temperature relation is of the form $\mu_T = \mu_0^{(a)} T^{-3/2}$ in the low temperature region and $\mu_T = \mu_0^{(\theta)} T^{-5/2}$ in the high temperature region. This is in very good agreement with the experimental results. We have analysed the concentration dependence of mobility by determining some of the constants using the experimental results given by Joffe et al. The theoretical curve (mobility versus concentration of one of the components) drawn shows the concentration dependence of the mobility. Further, it is found that the experimental points lie all along the theoretical curve.

Thus, we conclude that inter-band transition effects in the polar semiconductors, whether caused by optical phonons (or polar modes) or by alloying effects (in the case of solid solutions) play an important role in the electronic processes.

APPENDIX

In this appendix, we shall derive the crystal field potential on a metal ion in the solid solution PbTe-PbSe described by the model MX_fY_{1-f}. For this purpose, we follow the well known method of crystal field theory[71] and apply it to an octahedral cluster.

The atoms of the system are arranged in an octahedral configuration, with the metal ion M at the centre. The atoms X and Y are known as ligands and it is expedient to denote their positions in terms of polar coordinates (R_h, θ, ϕ). These are six ligands around M with the coordinates.

$$(R_h, 0, 0), \quad (R_h, \pi, 0), \quad (R_h, \pi/2, 0),$$

$$(R_h, \pi/2, \pi/2), \quad (R_h, \pi/2, \pi), \quad (R_h, \pi/2, 3\pi/2) \qquad \ldots\ldots. \quad (A.1)$$

respectively.

Let r be the position vector of an electron of the metal ion M. The electron moves in the electrostatic field V(r) produced by the surrounding ligands. For simplicity we treat the ligands as point charges.

It is convenient to expand V(r) in a series of normalised spherical harmonics as

$$V(\underline{r}) = \sum_{l=0} \sum_{m=-l}^{l} C_l^m \, r^l \, Y_l^m (\theta, \phi) \qquad (A.2)$$

Here, the coefficients C_l^m can be expressed in terms of the associated Legendre polynomials P_l^m. Thus,

$$C_l^m = \frac{Q}{R_h} P_l^m(\cos\theta)\left(\frac{1}{R_h}\right)^l \frac{2\sqrt{\pi}}{(2l+1)} {\frac{(l-|m|)!}{(l+|m|)!}}^{\frac{1}{2}} e^{\pm im\phi} \qquad (A.3)$$

where Q is the charge of the ligand in question. The total value of the coefficients C_l^m is obtained by summing the expression (A.3) over all point sources, using their respective coordinates as given by (A.1). The condition that the potential $V(r)$ must belong to the totally symmetric representation of the group of the unit (octahedral) determines as to which C_l^m are zero. We use the following values of l and m.

$$l = 0, 1, 2, 3, 4 \text{ and } m = -l \text{ to } l \qquad (A.4)$$

We place a Te^{--} ion at $(R\ 0\ 0)$ and Se^{--} ions at the remaining five coordinates. Let the point charge corresponding to Te^{--} be Q^1.

We shall now find the coefficients C_l^m for this configuration. One can easily see that out of the different values of l and m given above only the following coefficients survive:

$l = 0,\ m = 0 \qquad C_0^0 = \frac{Q}{R_h} 2\sqrt{\pi},\ \sum C_0^0 = \frac{2\sqrt{\pi}}{R_h}(Q^1 + 5Q)$

$l = 1,\ m = 0 \qquad C_1^0 = \frac{Q}{R_h^2}\frac{2\sqrt{\pi}}{\sqrt{3}}\cos\theta,\ \sum C_1^0 = \frac{2\sqrt{\pi}}{\sqrt{3}R_h^2}(Q^1 - Q)$

$$l = 2,\ m = 0 \qquad C_2^0 = \frac{Q}{R_h^3}\ \frac{2\sqrt{\pi}}{\sqrt{5}}\ \frac{3\ \mathrm{Cos}^2\ \theta - 1}{2}$$

$$\sum C_2^0 = \frac{2\sqrt{\pi}}{R_h^3\sqrt{5}} \left(Q^1 - Q \right)$$

$$l = 3,\ m = 0 \sum C_3^0 = \frac{2\sqrt{\pi}}{R_h^4\sqrt{7}} \left(Q^1 - Q \right)$$

$$l = 4,\ m = 0 \sum C_4^0 = \frac{\sqrt{\pi}}{3R_h^5} \left(2Q^1 + 5Q \right)$$

$$l = 4,\ m = \pm 4,\ \sum C_4^4 = \sum C_4^{-4} = \frac{Q}{3R_h^5} \sqrt{\frac{35\pi}{2}}$$

.... (A.5)

Thus substituting (A.5) in (A.2) we get

$$V(\underline{r}) = V_{lm}^{(p)} = \left(\sum C_0^0\right) Y_0^0\, r^0 + \left(\sum C_1^0\right) Y_1^0\, r^1$$

$$+ \left(\sum C_2^0\right) Y_2^0\, r^2 + \left(\sum C_3^0\right) Y_3^0\, r^3$$

$$+ \left(\sum C_4^0\right) Y_4^0\, r^2 + \left(\sum C_4^{\pm 4}\right) r^4 \left(Y_4^4 + Y_4^{-4}\right)$$

$$= \frac{(Q^1 + 5Q)}{R_h} + (Q^1 - Q) \left(\frac{z}{R_h^2} + \frac{3z^2 - r^2}{2R_h^3} + \frac{z(5z^2 - 3r^2)}{3R_h^4} \right)$$

$$+ \frac{(2Q^1 + 5Q)}{16R_h^5} (35z^4 - 30z^2r^2 + 3r^4)$$

$$\frac{35}{16}\ \frac{Q}{R_h^5} \left(x^4 + y^4 + z^4 - 6x^2y^2 \right)$$

...... (A.6)

Here x, y, z, are the coordinates of the electron in the cartesian system. Similarly replacing Se^{--} ion by Te^{--} at other coordinates, we can calculate the crystal field potential at the position of the electron.

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