Chapter - I

Introduction

The chalcogenides (sulfide, selenide and telluride) of transition metals show bonding characteristics intermediate between ionic and covalent. This results in a much larger varieties of structural and electronic properties among the chalcogenide compounds as compared to the largely ionic-bonding in oxides. Especially in case of dicahalcogenides of early transition metal, the covalent bonding results in anisotropic two dimensional (2D - layered) structures- with strongly bonded layers. These compounds permit intercalation – deintercalation of alkali metal atoms etc., in the weakly bonded Van der Waal’s gap in between the layers, by using electrochemical methods, and without losing the integrity of the structures. Thus they are extensively studied as potential materials for the rechargeable batteries for the high density of electrical energy storage and supply.

Many of these layered compounds especially of group IV (V, Nb and Ta) show an electronic transition on cooling. This transition is coupled to the distortions of the structure which is found to be commensurate, incommensurate or discommensurate with the periodicity of the lattice of the parent structure. This transition is due to occurrence of the Charge Density Wave (CDW) in the conduction electrons of the material and is theoretically predicted for the metallic phase with 1D and 2D- crystal structures. In the layered structures this CDW transition is very sensitive to stacking arrangement of the layers, the presence of the intercalate atoms in the Van der Waal’s gap and different lattice defects. For example a first order CDW transition of 1T-TaSe$_2$ (having single layered stacks) is observed at 473K but a second order CDW transition was found at 117K for 2H-TaSe$_2$ (with double layered stacks) [1].

Many of these layered compounds show superconducting properties at low temperatures. 2H- NbSe$_2$ shows a CDW transition at 38K and becomes superconductor (SC) around 7K [2, 3]. This is a remarkable behavior, since the superconducting order is not compatible with the CDW order. The possibility of the coexistence of the CWD phase and
superconductivity in anisotropic structures has been the subject of intense studied over the last four decades [4].

The large ranges of alloy-like and non-stoichiometric $M_pX_q$ compositions are possible for transition metal chalcogenides. The basic unit of a layer in the above mentioned $MX_2$ compounds has hexagonal CdI$_2$/CdCl$_2$ structure. The self-intercalation in $M_{1+x}X_2$: $0 < x < 1$ gives structures intermediate between CdI$_2$/CdCl$_2$ and NiAs type structure. In these compounds the Van der Waal's layers are progressively filled as 'x' is increased. These partially filled layers alternate with the filled layers. For the definite rational atomic ratio of metal and chalcogen atoms, vacancy ordered structures are obtained. These structures showed superstructure and distortions e.g. $V_5S_8$, $V_5S_4$ [5], $Nb_3S_4$, $Cr_3S_4$ etc either in the as-prepared phases or on cooling.

For the ternary Chalcogenides $A_xMX_2$ ($A =$ alkali metals or transition elements) the more common structures are above mentioned metal deficient NiAs – type with hexagonal symmetry or their vacancy ordered superstructures with trigonal, tetrahedral or orthorhombic symmetry. There are however, $A_xB_2X_4$: $x = 0$ or 1 compounds, (where $A=$ Cu, Ga, Al, Cd, Hg etc. $B =$ Ti, V, Nb, Cr, Fe, Ir etc.), which have spinel structures with cubic symmetry. These thiospinels exhibit very interesting physical properties. For example thiospinel of CuIr$_2$S$_4$ and CuV$_2$S$_4$ are metallic, the former showed a M-1 transition at 230K [6] and the later a CDW transition at 54K and 90K [7]. CuCr$_2$S$_4$ is a ferromagnetic metal below a transition at 430K [8], whereas HgCr$_2$S$_4$ and CdCr$_2$S$_4$ are magnetic semiconductors [9]. The compounds like Ga$_x$V$_2$S$_4$: $x = 0.5$ has a cubic structure which are derived from the spinel structure. Here the transition metal atoms (V-atoms) on the B-sites of spinel-lattice form tetrahedral clusters [10]. These are Mott –insulators and show ferromagnetic transition below 25K.

1.1 Transition Metal Dichalcogenides (MX$_2$)

The loosely coupled X-M-X sheets in MX$_2$ ($M =$ group IV, V and VI transition elements), makes the compound extremely interesting. The more ionic compounds of
groups VII and VIII form non-layered compounds. In layered compounds the bonds are very strong in a layer but between the layers the Van der Waal's bonds are very weak. Electrically they cover wide spectrum of properties as: insulator like HfS₂, true metal like NbS₂ and VSe₂ and semiconductor like MoS₂.

1.1.1 Layered Compound

Within a single X-M-X layer, the M and X atoms form two dimensional hexagonal arrays. Depending on the relative alignment of the two X-atom sheets within a single layer of X-M-X, two different layer structures either, CdI₂ or CdCl₂-type as well as a mixture of these two are possible. In one, the metal atoms are octahedrally coordinated by six nearest neighbors X-atoms whereas in the other, the co-ordination of the metal atom is trigonal prismatic. In layered structure different polymorphs/polytypes are found depending on the preparative conditions. According to Wijckhoff [11] there is a distinction between the CdI₂ and CdCl₂ structure. The CdI₂ structure has an almost perfect hexagonal close packing (ABABA-----) of the anions with the metal atom in octahedral intertices. But in CdCl₂ structure the octahedral surrounding is retained, the close packing is cubic (ABCABCA----) rather than hexagonal.
1.1.2 Polymorphs and polytypes

The layers of MX₂ (i.e. called slab) are stacked along the z-direction by the weak interlayer Van der Waal’s force. The number of slabs indicates the thickness of the repeat unit cell in the z-direction and the symmetries are denoted by the T, H and R for Trigonal, Hexagonal and Rhombohedral respectively. The metal atom ‘M’ can be coordinated with the six chalcogen atoms in two different ways as follows: octahedrally co-ordination (AbC) or trigonal prismatic co-ordination (AbA) in two dimensional layered compounds as shown in fig. 1(b) and (c). There is more than one stacking order possible along the c-axis to form the different polymorphs of MX₂ are 1T, 2H, 4H and 3R etc. whereas 2Ha, 2Hb and 2Hc and 4Ha, 4Hd₁, 4Hd₂ etc. represent different polytypes. The detail stacking orders and space groups of MX₂ are shown in Fig. 1.2.

The one slab structure is possible for octahedral surrounding of the metal atom but the one slab structure is not known for prismatic surrounding of the metal atom due to the unstable lattice. The two-layered structure of MX₂ exists in three different ways of stacking the slabs as follows: AbA/CbC for 2Ha-MX₂, AbA/BaB for 2Hb-MX₂ and AbA/BcB for 2Hc-MX₂. Only one three layers stacking was found for 3R-MX₂ as
AbA/AbC/CaC. The packing of four layers of MX$_2$ has alternating prismatic and octahedral surrounding of metal atom like AcA/BcB/AbC/CbC for 4Ha-MX$_2$, AbA/AbC/CbC/BaC for 4Hd-MX$_2$ and AbC/AbC/AbC/CbC for 4Hdu-MX$_2$ was found.

Fig. 1.2: (110) section of various polymorphs and their polytypes shown in different stacking scheme and the co-ordination of MX$_2$.
1.1.3 Intercalated compounds

When the foreign atoms or molecules are incorporated into the Van der Waal’s gap without disturbing the parent structure, process is called intercalation of the atoms. Since the structure is not disturbed, one can discuss the changes in the electronic properties of intercalated compounds in terms of the transfer of electrons from the intercalated atom to the rigid bands of the parent phase. The progressive filling of the bands one can lead to metal-to-semiconductor or semiconductor-to-metal transitions on intercalation. Many intercalated compounds can become superconductor at low temperatures. In the process of intercalation, the structure of an existing crystal can also be modified with the sharp changes in the electronic properties. According to the Liang the intercalated compounds fall into three broad categories depending on the intercalant species [12].

1. Alkali metals of Li, Na, K, Ru, Ag, Ca, In and Pb etc.
2. Organic molecules of Amines, Amides, Pyrides, Ammonia and Hydrazine.
3. Transition metal atoms of V, Cr, Mn, Fe, Co, Ni and many other non-simple metals of Europium and Gadolinium.

1.1.4 Band model

The band structures are directly related to the geometry of the structure and vice-versa. This can be seen by the effect of co-ordination on the chalcogen environment from octahedral for group-IV metals and trigonal prismatic for group VI metals. But in group-V transition metals, both the co-ordinations are possible.

Wilson and Yoffe [13] have described in a general scheme the electronic structures of dichalcogenides. According to them, the s and p orbitals of the chalcogen atoms are divided into occupied (\(\sigma\)) and unoccupied (\(\sigma^*\)) bands, separated by an energy gap of several eV. The d-band of the transition metal atoms present in the octahedral co-ordination is located within the bonding and antibonding energy gap. Then the d-band
splits into a two fold degenerate level $e_g$ associated with $d_{yz}$ and $d_{zx}$ orbitals and into a threefold degenerate level $t_{2g}$ associated with $d_{z^2}$, $d_{xy}$ and $d_{x^2-y^2}$ orbitals. Again this low lying degenerate level is split into singly occupied $d_{x^2}$ orbital and doubly occupied $d_{xy}$ & $d_{x^2-y^2}$ orbitals in the trigonal prismatic co-ordination due to the low Madelung energy. The electric, magnetic and optical properties are related to the filling of the d-band electrons.

Fig. 1.3: Schematic band model of group IV, V and VI element with different coordinations [Ref. 13].

This can be understood by simple ionic picture, where two electrons are transferred from the transition metal atoms to fill the outer p-orbitals of the chalcogen atoms. Then the remaining outer d-band electrons of the transition metals play the role of various properties of the compounds. The transition metals of group-IV are in $d^0$ configuration. giving d-band empty, the respective transition metal dichalcogenides (TMDC) are generally semiconductor. TMDC of group-V elements (V, Nb and Ta) has half filled $d_{z^2}$ band, resulting the metallic behavior. But the $d_{z^2}$ band is completely filled for group-VI metals showing the semiconducting properties.
1.2 Ternary Transition Metal Chalcogenides (AM$_2$X$_4$)

Ternary transition metal chalcogenides with the chemical formula AM$_2$X$_4$ (A, M = transition metal, X = S, Se and Te) generally adopt either cubic spinel structure or cation-deficient NiAs-type hexagonal structure. The metal ions and polarizability of the anions determine which of these structures is favored. The metal ions occupy both the tetrahedral and octahedral interstices in the cubic close-packed array of anions in the thiospinel lattice. But in the hexagonal close-packed array of anions in NiAs type structure, the metal ions occupy only octahedral interstices. In the spinel structure, the tetrahedral and octahedral interstices are stabilized by divalent, trivalent and quadrivalent cations. When both the cations are stabilized on octahedral interstices, the NiAs-type structure can form. Increasing the anion polarizability in the sequence S < Se < Te increases the octahedral site stabilization, which favors the formation of NiAs-type structure.

1.2.1 Thiospinel Compounds (AM$_2$X$_4$)

The thiospinel AM$_2$X$_4$, (where A, M = transition metal atom, X = S, Se and Te) having FCC lattice of space group Fd3m and exhibiting a large variety of physical properties, which makes them interesting for scientific point of view. The near-neighbor atomic d-orbitals of the transition metal atoms in thiospinels overlap with larger extent than in oxides, the conduction process in these materials are occurred by the collective-d electrons. The oxyspinels are generally semiconductors with antiferromagnetic interactions. But thiospinels also exhibit metallic conduction (e.g. CuTi$_2$S$_4$, CuCo$_2$S$_4$ and CuV$_2$S$_4$) and superconduction (e.g. CuRh$_2$S$_4$ below 4.8K and CuRh$_2$Se$_4$ below 3.5K). ZnCr$_2$S$_4$ is anti-ferromagnetic semiconductor. CuCr$_2$S$_4$ and CuCr$_2$Se$_4$ are metallic ferromagnets below 460K [8].
1.2.2 Spinel Structure

Spinel belongs to the space group Fd3m having symmetry FCC.

The co-ordination numbers are as follows:

<table>
<thead>
<tr>
<th>A</th>
<th>M</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>16d</td>
<td>32e</td>
</tr>
</tbody>
</table>

- **A**, tetrahedral (AX₄)
- **M**, octahedral (MX₆)
- **X**, tetrahedral (XAM₃)

**Table - 1.1**

Atomic coordinates of the spinel AM₂X₄

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Fractional coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8a</td>
<td>000, ½ ½ ½ + face centering</td>
</tr>
<tr>
<td>M</td>
<td>16d</td>
<td>⅛ ⅛ ⅛; ⅛ ⅛ ⅛; ⅛ ⅛ ⅛; ⅛ ⅛ ⅛ + Face centering</td>
</tr>
<tr>
<td>X</td>
<td>32e</td>
<td>uuu; uuu; uuu; uuu; ½-u, ½-u, ½-u; ½+u, ½-u, ½-u; ½-u, ½+u; ½+u, ½+u, ½-u; + face centering</td>
</tr>
</tbody>
</table>

Fig. 1.4: F.C.C. Spinel structure with octahedral and tetrahedral co-ordination of 'M' and 'A' transition metal atoms. (The red cubes are also contained in the back half of the unit cell).
The unit cell of spinel contains eight formula units corresponding to $A_8M_{16}X_{32}$. The atoms are three sets of special positions as mentioned earlier. The 'A' atom is an eight fold set, label 8a: co-ordination of two positions are given in table -1.1 at (0,0,0) and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

The remaining six are generated by the face centering operation, i.e. for an atom at position $(x, y, z)$ there are three other identical atoms at the equivalent positions of $(x + \frac{1}{2}, y + \frac{1}{2}, z)$, $(x + \frac{1}{2}, y, z + \frac{1}{2})$ and $(x, y + \frac{1}{2}, z + \frac{1}{2})$. The six other 'A' ions are therefore at $(\frac{1}{2} \frac{1}{2} 0)$, $(0 0 \frac{1}{2})$, $(0 \frac{1}{2} 1)$, $(\frac{1}{2} \frac{1}{2} 1)$, $(1 \frac{1}{2} \frac{1}{2})$ and $(\frac{1}{2} 1 \frac{1}{2})$. Similarly the rest twelve positions of the 'M' ions are generated by face centering operation using the co-ordination of four positions $(\frac{1}{8} \frac{1}{8} \frac{1}{2})$, $(\frac{3}{8} \frac{3}{8} \frac{3}{2})$, $(\frac{5}{8} \frac{5}{8} \frac{1}{2})$ and $(\frac{7}{8} \frac{7}{8} \frac{3}{2})$. The arrangement of the sulphide ions is ideally cubic close packed if the $u$ parameter has the value $\frac{1}{8}$. Thus the 32 positions of the 'X' ions are generated by face centering operation using the value of $u = \frac{1}{8}$.

A complicating factor in the spinel structure is that the cation distribution over the 8a and 16d sites may vary. In normal spinel, the cations are in the sites that would be expected from the formula $AM_2X_4$ i.e. with 'A' in tetrahedral 8a sites and 'M' in octahedral 16d sites. In inverse spinel, half of the 'M' ions are in tetrahedral 8a sites leaving the remaining 'M' ions and 'A' ions to occupy the 16d sites. Usually the occupancy of these 16d sites is disordered.

$$\text{Normal Spinel: } [A]^\text{Tet} [M_2]^\text{Oct.} X_4$$

$$\text{Inverse Spinel: } [M]^\text{Tet} [AM]^\text{Oct.} X_4$$

### 1.2.3 Insulating $M_4$-Cluster compounds ($AM_4X_8$)

The cluster compounds belong to the ternary transition metal chalcogenides of the composition $AM_4X_8$, ($A = \text{Ga and Ge, } B = \text{Mo, Nb, V and Cr and } X = \text{S, Se and Te}$) having FCC lattice. This FCC structure is a deficient spinel $A_{0.50}M_2X_4$ compound in which the ordering of tetrahedral 'A' sites reduces the space group from Fd3m to $F43m$. 

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The octahedral $M_4$ cluster form within $M_4X_4$ units, where the intra-cluster distance between $M-M < 3\AA$ and inter-cluster distance $M-M \geq 4\AA$. The cluster $M_4 (M = V, Nb, Cr)$ contains seven valence electrons but $M = Mo$ contains eleven valence electrons indicates one unpaired electron per cluster is responsible for magnetic properties. The interesting aspect of these compounds is that they are Mott insulators and here the conduction occurs through hoping of the charge carriers between the well separated ($> 4\AA$) $M_4$-metal clusters. This leads to strong correlation effects between localized electronic states and magnetic properties at low temperature.

$Mo_4S_4I_4$ is diamagnetic [14], $GaNb_4S_8$ and $GaTa_4S_8$ are paramagnetic [15] and $GaV_4S_8$ is ferromagnetic below 13K [16]. M. M. Abd-elmeguid et al. observed the transformation of non-magnetic Mott insulator of metallic and superconducting state for $GaM_4Se_8 (M = Nb, Ta)$ cluster compounds at the pressure of 13GPa and 11.5GPa with the critical temperature of $T_c = 2.9K$ and 5.8K respectively [17].

1.2.4 $(Fd3m\leftrightarrow Fd\bar{4}3m)$ Transformation

The lowering of the cubic symmetry brings the following relaxations in the spinel structure. The 8a equivalent tetrahedral cations of $Fd3m$ split into two non-equivalent sets of four each at $4a(0,0,0)$ and $4c(4,4,4)$ called $T_1$ and $T_2$ respectively. The ordering of $T_1$ and $T_2$ in the $Ga_0.50Mo_2S_4$ gave the weak relative intensities of the 200, 600, 420 and 640 planes in the X-ray diffraction patterns. The $16d(t, t, f)$ octahedral cations of the spinel shift from their ideal positions to $16e(u,u,u)$, resulting the tetrahedral cluster compounds of $V_4$, $Nb_4$, $Mo_4$ and $Cr_4$ etc. The parameter ‘u’ deviates from $u > 5/8$ to form the two pseudo-cubic units $C_1$ and $C_2$ in the spinel. The $32e(u,u,u)$ anions of the spinel compound are also divided into two parts of $16e(x,x,x)$, $x = \frac{5}{8}$ and $16e(x,x,x)$, $x = \frac{7}{8}$ in cluster compound. The formation of cluster in the ternary transition metal chalcogenide compounds arise from different mechanism. For example the formation of cluster in $Ga_{0.50}Mo_2S_4$ spinel is due to the occupied and vacant sites of the tetrahedral positions at $T_1$ and $T_2$ by Ga respectively [10]. But in $CuV_2S_4$, the cluster was formed.
below the 90K is due to the periodic lattice distortions (PLD) of the octahedral cations due to the CDW formation [7].

![Tetrahedral cluster of V-atoms in GaV₄S₈](Ref. 17)

**1.3 Superconductivity/Charge Density Wave (CDW)**

N. Tsuda et al. [18] in their book “Electronic conduction in oxides” described how the transitions from metallic to charge density wave (CDW) and superconducting (SC) states are related to the competitions between itinerancy (intersite transfer energy integral T) and electron-phonon coupling energy (S). The effect of the T and S competition on the electronic interaction is very different from the coulombic repulsion U. In the case of phonon mediated inter-electron interaction, the quantum of phonon energy (ω) is exchanged and because of the finite velocity of the phonons the interaction is retarded.
This, under favorable condition gives attractive interaction and formation of cooper pairs and superconducting transition. The net attraction between the electrons depends strongly on ratio between T and ω. For T >> ω, the phonons can not follow the motions of the electrons at all, but can give only a static potential due to a frozen local lattice distortion. This is called adiabatic in which the electron will be trapped in the local lattice distortion since it can follow the motions of phonons completely. This condition is favorable for self trapping and CDW transition. But for T << ω, the phonons can follow the motions of the electrons instantaneously, resulting in an attraction with no retardation, just like the columbic force. This can be called inverse adiabatic.

When the coupling is weak, S << T, the relative stability between the CDW state and the SC state is mainly determined by the geometric shape of the unperturbed Fermi surface. In the SC state the energy gap can be opened all over the Fermi surface irrespective of its geometric shape while in the CDW state, it can be opened only in two parts of the Fermi surface, that can be nested with respect to each other by a certain phonon wave vector and other part of the Fermi surface are left unchanged. If such a nesting area is very wide as in the case of cubic/square Fermi surface, the CDW always becomes stable. But if the nesting is absent as in the case of a spherical surface, the SC state is always stable.

In the case of strong coupling, S >> T, the relative stability between the two phases is insensitive to the geometric shape of the unperturbed Fermi surface, since the one-electron energy band itself is greatly altered from the original one. For the strong coupling and adiabatic case, ω << T << S, self trapping of electrons or the CDW transition appears but for strong coupling and inverse adiabatic, ω >> S >> T, is the origin of the superconductivity.
1.4 Hopping Conduction

In disordered systems, when the condensed electronic states are localized near the Fermi level $E_r$, the electronic conduction does not obey the rule of normal metal but follow the Variable Range Hopping (VRH) theory of Mott [19, 20]. According to this theory, the hopping conduction takes place between the localized states of electrons whose wave functions are overlapped to each other. Every time one localized electron is jumped from an initial site ‘i’ to the nearest site ‘j’ with the minimum energy $\Delta W$ above it.

$$\frac{4}{3} \pi R^3 \int_{E_{\mu}}^{\text{E}_{\mu+\Delta W}} N(E) dE = 1$$

or

$$\Delta W = \frac{3}{4 \pi R^3 N(E)}$$

Then the hopping probability between the localized sites depend on two factors.

Fig. 1.6: Formation of band gap at the Fermi level related to the PLD.
1. Boltzmann factor: \( \exp\left\{-\frac{\Delta W}{K_B T}\right\} \)

2. Factor depending on the overlap of the wave functions: \( \exp\{-2\alpha R\} \)

Where, \( K_B \) = Boltzmann constant

\( T \) = Temperature

\( R \) = Distance separating sites

\( \alpha \) = Wave function decay length

Then the conductivity behaves as the factor of \( \exp\left\{-2\alpha R - \frac{\Delta W}{K_B T}\right\} \) quantity expressed as,

\[
\sigma = \sigma_0 \exp\left\{-2\alpha R - \frac{\Delta W}{K_B T}\right\}
\]

(1.4b)

Where, \( \sigma_0 \) is the weakly temperature-dependent factor. The idea of the Mott theory of \( T^{-1/4} \) was to maximize the hopping probability. In other words it turns to minimize the equation (1.4b) to get the minimum hopping distance in 3-dimension case,

\[
\bar{R}_{3D} = \left\{\frac{9}{8\pi\alpha N(E_f)K_B T}\right\}^{1/4}
\]

(1.4c)

This equation indicates the enhancement of hopping distance between the localized electronic states on going down to the lowest temperature.

On substituting the energy \( \Delta W \) required to hop between the localized states of minimum distance \( \bar{R}_{3D} \) in equation (1.4b), we get the familiar Mott equation of conductivity in 3-dimensions.

\[
\sigma_{3D} = \sigma_0^{3/4} \exp\left\{-\left(\frac{T_0}{T}\right)^{1/4}\right\}
\]

(1.4d)

Where, \( K_B T_0 = \frac{e^4 \alpha^3}{N(E_f)} \)

The minimum energy required to hop the electronic localized sites can be derived as a function of temperature by putting the \( \bar{R}_{3D} \) in equation (1.4a).
\[ \Delta W = \left\{ \frac{3}{4\pi N(E_f)} \right\}^{\frac{1}{4}} \left\{ \frac{2\alpha K_n T}{3} \right\}^{\frac{3}{4}} \]  

(1.4e)

This equation indicates the energy required to hop between the localized electronic states are decreases with the temperature decreases. Again the critical temperature was calculated by using the value of \( R \) from equation (1.4a) in equation (1.4c) up to which the Mott equation is valid

\[ T_c = \left\{ \frac{9}{8\pi \alpha N(E_f) K_n} \right\}^{\frac{3}{4}} \left\{ \frac{3}{4\pi N(E_f) K_n \Delta W} \right\}^{\frac{3}{4}} \]  

(1.4f)

The conductivity expression derived for Variable range hopping (VRH) was valid for the constant \( N(E) \) density of states (DOS) near the Fermi energy. But when the \( N(E) \) was zero the conductivity of the equation (1.4d) was changed. Thus the density of localized states (DOS) near the Fermi energy can be written as \( N(E) = c|E - \mu|^{\alpha} \). Then the conductivity of the disordered systems for \( N(E) \neq \) constant was calculated as follows,

\[ \frac{4}{3} \pi R^3 \int_{\mu}^{\mu+\Delta E} N(E) dE = 1 \]

or

\[ \Delta W = \left\{ \frac{3(n+1)}{4\pi c} \right\}^{\frac{1}{n+1}} \left( \frac{1}{R} \right)^{\frac{3}{n+1}} \]  

(1.4g)

Then the minimum distance of hopping between the localized sites was derived from the equation (1.4b) and (1.4g) as follows,

\[ \bar{R}_{3D} = \left\{ \frac{3(n+1)}{4\pi c} \right\}^{\frac{1}{n+4}} \left\{ \frac{3}{2\alpha(n+1)K_n T} \right\}^{\frac{n+1}{n+4}} \]  

(1.4h)

Then the Conductivity at the low temperature was calculated by using the as follows,
\begin{equation}
\sigma = \sigma_0 \exp \left\{ - \left( \frac{T_0'}{T} \right)^{n+4} \right\} \tag{1.4i}
\end{equation}

Where, \( T_0' = \left( \frac{C^{n+1}}{\alpha^3} \right)^{\frac{1}{n+1}} \)

Then Efros and Shklovskii (1975) showed the hoping conduction of the interacting carriers (i.e. Coulomb repulsion) for \( n = 2 \) in equation (1.4i).

\begin{equation}
\sigma = \sigma_0 \exp \left\{ - \left( \frac{T_0'}{T} \right)^{\frac{1}{2}} \right\} \tag{1.4j}
\end{equation}

Where, \( K_\beta T_0' = C^{1/3} \alpha \)
References