Theory of high pressure studies on low-dimensional conductors

A T Oza & P C Vinodkumar
Department of Physics, Sardar Patel University, Vallabhidyanagar 388 120
E-mail: ajayozat@yahoo.com

Received 7 January 2008; revised 15 September 2008; accepted 14 November 2008

The behaviour of the experimentally observed electrical resistivity of organic semiconductors, single crystals of polycrystalline chain complexes and the nickel organo metallic compounds under pressure have been explained theoretically by considering various physical processes related to these compounds. The pressure dependence of the various transport parameters such as the mobility, effective mass of the charge carriers and the mean collision time etc are also deduced from the experimental behaviour through the theoretical modeling.

Keywords: Low dimensional conductors, Electrical resistivity, High pressure, Beta density, Transport properties

1 Introduction

There is renewed interest in the field of organic, organo-metallic and polymeric low dimensional conductors, particularly at different physical conditions such as temperature and high pressures1-5. The high-pressure studies are important in the field of elemental and compound semiconductors such as ZnS6, CdTe/CdMgTe heterostructures7, potassium and rubidium dihydrogen phosphates8, zinc blende aluminium nitride and gallium nitride9, YbPd5S1210, ZnTe11, GaP and GaN12. Many interesting high pressure studies on different compounds are available6. Despite the fact that there exist many high-pressure experimental studies on metals and semiconductors, there are few theoretical attempts to understand the behaviour of electrical and optical properties of low dimensional conductors under pressure. In this study, the experimental data on the electrical properties of inclusion compounds and charge transfer complexes under high pressure (up to 80 kbars) have been interpreted using theoretical concepts.

The pressure dependence of the ac/dc resistivities of some organic semiconductors, namely α-cyclo-dextrin–KI–I2–4H2O, amylose–iodine, (coumarin)4–KI–I2, DTN (dithionaphthalene), DTN–I2, anthracene–TNB (TNB = trinitro benzene) and pyrene–2I2 were experimentally studied earlier13-18. The experimental results of these dc/ac electrical resistivities of several low – dimensional conductors under pressure have been employed in the present study to develop theoretical understanding of different physical processes occurring within such compounds19. Compounds, particularly the charge transfer complexes mentioned above were found to obey either \( \rho/\rho_0 = A + BP^* \) \( \frac{1}{2} \) \( 1-P^* \) \( \frac{1}{2} \) or \( \rho/\rho_0 = A + BP^* \) \( \frac{2}{2} \) \( 1-P^* \) \( \frac{2}{2} \). Here, \( P^* = (P-a)/b \), \( a \) is due to arbitrary zero of the process and \( b \) is the base width of the resistivity peak. The dc resistivities of the single crystal inclusion compounds of iodine obey, \( \frac{\rho - \rho_0}{\rho_0} = A + \frac{K(P-A)}{1+bP} \exp \left[ -C \left( \frac{P-A}{K} \right) \right] \exp \left( \frac{-CA}{K} \right) \) relation. The organometallic compounds such as nickel dimethyl glyoxime \([Ni(Hdmg)_2]\) and nickel diphenyl glyoxime \([Ni(Hdpg)_2]\) follow gaussian distribution in pressure dependence of resistivity19. An attempt has been made to understand these behaviours of resistivity of the low-dimensional conductors under pressure based on the theory of the transport properties of semiconductor materials. The classical, semi-classical and quantum mechanical approaches have been employed in the present study.

Kinematics of charged particles under the action of different external fields can be understood classically through Maxwell-Boltzmann statistics. Kinetic theory of gases can be applied to electron gas as well. The velocity distribution of charge carriers is important in the understanding of the transport phenomena in solids. So, as a classical treatment the desired functional forms for the electrical dc resistivity from the Maxwell-Boltzmann distribution have been derived in this study. The theoretical approaches of the study are applicable not only to the low-dimensional conductors but also to metals, semi-
conductors and ionic materials where similar pressure dependencies have been observed.

2 Theory
2.1 Transport properties and Maxwell-Boltzmann distribution

The Maxwellian distribution deals with the distribution of particles having different velocities, i.e. how particles are distributed in a range of classical (non relativistic and non quantum - mechanical) velocities in the neighbour of the average velocity. Charge carriers such as the electron gas can be described with such a distribution. When the material is a large band gap semiconductor, the number density of the charge carriers in the conduction band is very less. So, the charge carriers (electrons, holes, polarons, etc.) responsible for the electrical conductivity can be assumed as a dilute gas having low enough density to neglect the coulomb repulsion.

The resistivity of a material is related to the carrier density (n) and mobility (µ) as:

$$\rho = \frac{1}{en\mu}$$  \hspace{1cm}  \text{(1)}

The classical distribution for the charge carriers is given by:

$$n_i = \frac{1}{g_i} \exp(\alpha + \beta \varepsilon_i)$$  \hspace{1cm}  \text{(2)}

Here, the parameter α is related to the chemical potential, which depends on particular carrier particles. For the electron gas, it is given by:

$$\alpha = -\frac{2\pi \hbar^2}{m_e K_b T} \left( \frac{3 \rho \sqrt{\pi}}{4 g_{m_e}^2} \right)^{2/3} \text{ and } \beta = \frac{1}{K_b T}$$  \hspace{1cm}  \text{(3)}

For a classical gas, the chemical potential is equal to zero. So α = 0, ε_i = 1/2 m_i v_i^2 and Eq. (2) becomes the Maxwellian distribution. In one-dimensional case, it is given by:

$$dn = N \left( \frac{m^*}{2\pi K_b T} \right)^{1/2} \exp \left( -\frac{m^* v^2}{2 K_b T} \right) dv$$  \hspace{1cm}  \text{(4)}

Substituting Eq.(4) in Eq. (1), gives:

$$\rho = \frac{2 \pi K_b T}{e (dn / dv) \mu} \exp \left( -\frac{m^* v^2}{2 K_b T} \right)$$  \hspace{1cm}  \text{(5)}

Comparing with the experimental dependence of the resistivity on pressure for iodine chain complexes gives:

$$\rho / \rho_0 = A + \frac{K (P - A)}{1 + b P} \exp \left[ C \left( \frac{P - A}{K} \right) \exp \left( -\frac{CA}{K} \right) \right]$$  \hspace{1cm}  \text{(6)}

for crystals and

$$\rho = K P \exp ( -CP )$$  \hspace{1cm}  \text{(7)}

for pellets.

Eq. (7) can be related to the three dimensional Maxwellian distribution in velocity, if we consider $P = 1 / 3 m^* n^2 v^2$. So, pressure changes the velocity of the charge carrier and tracks the Maxwellian distribution. However, the relation given by Eq. (6) can be correlated with shifted Maxwellian distribution by identifying $\frac{A}{K} = \frac{P_0}{1 / 3 m^* n_0^2 v_0^2}$, while the pressure term in the denominator arises from the variation of mobility with pressure.

The crystalline anisotropy and the increase in the anisotropy caused by the applied pressure on oriented crystals are sufficient to create a pressure induced Peierls transition in which the kinetic energy of charge carriers suddenly reduces. The potential energy increases due to the screened coulomb interaction by the same amount.

Eq. (5) also leads to square power beta density

$$\frac{\rho}{\rho_0} = A + B \rho^2 (1 - P^*)^2$$  \hspace{1cm}  \text{(8)}

where, $P^* = (P - a) / b \rho$, when $\frac{\partial n}{\partial v} \sim P - P_0$, $\mu \sim 1 / P$ and $v^2 \sim P$ or $\frac{\partial n}{\partial v} \sim P$, $m^* \sim P^2$, $\mu \sim (P - P_0)$ and $v^2 \sim P - P_0$, as found in anthracene-TNB and pyrene-2I2 crystals. Similarly the half power density,

$$\frac{\rho}{\rho_0} = A + B \rho^{1/2} (1 - P)^{1/2}$$  \hspace{1cm}  \text{(9)}
Is obeyed when we consider the relation \( \mu = \frac{e\lambda v}{m v} \),
with \( \lambda \sim \) constant, \( m^* \sim (P - P_0)^2 \), \( \frac{\partial n}{\partial v} \sim P - P_0 \) and 
\( v \sim (P - P_0)^{3/2} \) as found in DTN and DTN-I\(_2\) compounds. The Gaussian distribution in pressure is

\[
\frac{\rho}{\rho_0} = A + B \exp\left(-\frac{(P - P_0)^2}{2M_2}\right) \quad \ldots (10)
\]

By considering \( v \sim \) constant, \( m^* \sim (P - P_0)^2 \),
\( \frac{\partial n}{\partial v} \sim P - P_0 \) and \( \mu \sim \) constant, as found in nickel dioximes\(^{19}\).

### 2.2 Energy fluctuation and non-equilibrium processes under pressure

External pressure applied on a semiconducting material leads to a non-equilibrium in filling of the density of states by the charge carriers. This induces an energy fluctuation because of change in the Fermi level or demarcation level (a level in the traps in the forbidden energy gap, which differentiates between ordinary traps and recombination centers) just the way radiation affects the Fermi level in a photoconductor and generates non-equilibrium\(^{21}\). The charge density waves (CDW) have been considered in conducting one-dimensional system, which undergoes a fluctuation in energy and the number of charge carriers, phonons or polarons do not change under the application of external pressure. This is consistent with an earlier description of high-pressure data on the inclusion compounds of iodine where the changes in the depths of the traps were considered rather than change in the density of traps or density of defects\(^{14}\).

The electrical resistivity is related to the energy as:

\[
\rho = \frac{m^* v}{n e^2 \lambda v} = \frac{\hbar k^2}{n e^2 v} = \frac{2m^*}{n e^2 h v} < E - U > \quad \ldots (11)
\]

where \( k \) is the wave vector of CDW and \( \lambda = l/k \) is the wavelength of CDW. The mean free path is limited by \( \lambda_{max} = \lambda_{CDW} \). Now making use of the fact that the distribution of energy among systems in the canonical ensemble is given by the gaussian\(^{22}\) with mean value \( U \) and dispersion \( \sqrt{K_b T^2 C_v} \), \( < E - U > \) can be obtained as:

\[
< E - U > = \int (E - U) P(E) dE \quad \ldots (12)
\]

where the canonical energy distribution is given by\(^{22}\):

\[
P(E) = \exp\left[ -\beta (U - TS) \right] \exp\left[ -\frac{(E - U)^2}{2K_b T^2 C_v} \right] \quad \ldots (13)
\]

After the integration of Eq. (12) using Eq. (13), the resistivity given by Eq. (11) becomes:

\[
\rho = \frac{B m^*}{n_0 e^2 h v} \exp\left[ -\beta (U - TS + E_0) \right] \exp\left[ -\frac{(E - U)^2}{2K_b T^2 C_v} \right] \quad \ldots (14)
\]

Here, the carrier concentration \( n \) is expressed as \( n_0 \exp(-E_0/K_b T) \).

The \( (E-U) \rightarrow (P-P_0) \) results into the gaussian behaviour in pressure observed for the resistivity in certain organometallic compounds. Here, a canonical ensemble of optical phonons is considered which interacts with the electrons, for which \( \omega \) is proportional to \( P \).

If the probability function \( P(E) \) is expanded to keep only the first term in the integration of Eq. (11), we get

\[
\rho \propto \frac{B m^*}{n v K_b T^2 C_v} (E - U)^2 \quad \ldots (15)
\]

and if \( m^* \rightarrow P^2 \), \( (E-U) \rightarrow (P-P_0) \) and \( n v \) is independent of the external pressure, the desired square power beta density function, \( P^2 (P-P_0)^2 \) is obtained. On the other hand, if \( n v \) also depends on the applied pressure as \( P^{1/2} \) or \( (P-P_0)^{1/2} \), the half power beta density, \( P^{1/2} (P-P_0)^{1/2} \) is obtained, as observed in some compounds.

For the cases where the fluctuation \( E-U \) is very small such that the gaussian term in Eq. (14) becomes unity and under moderate pressure, \( U+E_0/e \rightarrow E^0 \cdot C P, m^* \rightarrow P^2, \quad v \rightarrow P/(1+bP) \) lead to the form

\[
A + \frac{K}{K_b} \exp(-CP) \]

A + \frac{K}{1+bP} \exp(-CP) for the resistivity of the single crystal inclusion compounds of iodine.

### 2.3 Diffusion mechanisms and resistivity under pressure

In ordered systems, the hopping process is a Brownian motion. In markovian limit, the correlation
function in the Langevin equation is a δ-function
while in the non-markovian case, δ-function is
smeared out in time scale and corresponds to the
collision time. For disordered systems, the diffusion
function \( P(r,t) \) has a non-markovian form leading to a
spread. For sufficiently long collision time, the
diffusion function in one dimensional conductors,
\( P(x,t) \) describes a Gaussian behaviour as \( ^{23} \):

\[
P(x,t) = (\pi D t)^{-1/2} \exp(-x^2 / 4 D t) \quad \ldots (16)
\]

Now as in Eq.(11), the resistivity \( \rho \) is expressed as

\[
\rho = \frac{m^* v}{n e^2 \lambda v} \frac{1}{n e^2 \lambda v} \int (p - p_0) P(p,t) dp \quad \ldots (17)
\]

where \( P(p,t) \) is the momentum representation of
Eq. (16) given by

\[
P(p,t) = (D t / \pi)^{1/2} \exp[-D t (p - p_0)^2] \quad \ldots (18)
\]

Using Eq. (18), integrating Eq. (17) gives

\[
\rho = \frac{1}{2 n e^2 \lambda v D t} \exp[-D t (p - p_0)^2] \quad \ldots (19)
\]

The time \( t \) has an upper bound given by the collision
time or the relaxation time \( \tau \). As \( t \to \tau, \rho \to \) a fixed
equilibrium value. Considering that the carrier
concentration under the external pressure \( P \), goes as \( n \sim n_0 \exp[-(E_g^0 - \lambda P)] \), Eq. (19) becomes:

\[
\rho = \frac{\exp(E_g^0 / 2 K_B T)}{2 n_0 e^2 \lambda v D t} \exp[-D t (p - p_0)^2 - \alpha P] \quad \ldots (20)
\]

It is now similar to Eq. (14) except for the \( m^* \)
dependence. It can further be written as:

\[
\rho = \frac{\exp \left[ E_g^0 / 2 K_B T - D t (p_0^2 - p_0^2) \right]}{2 n_0 e^2 \lambda v D t} \exp[-D t (p - p_0^2)] \quad \ldots (21)
\]

where \( p_0 = p_0 - \frac{\alpha}{2 D t} \)

Now consider the momentum \( (p-p_0) \) proportional to
applied pressure \( P \), and relate the diffusion coefficient
\( (D) \) with mobility as:

\[
\mu = e D / K_B T = e \lambda v / p \quad \ldots (22)
\]

If we assume that diffusion time \( t \equiv \tau = 1/ \nu \) and \( \lambda / p \)
is independent of pressure, then \( D t \) becomes pressure
independent quantity. Thus, Eq. (21) leads to the
gaussian form as observed in Ni – compounds.

To explain the pressure behaviour on the resistivity
of the iodine complexes within the diffusion
mechanism, consider the applied force \( F = PA = \frac{dp}{dt} \),
where area \( A \propto P \) and the relaxation time \( \tau \propto P^{-3/2} \)
such that, the momentum \( p \) is proportional to \( P^{1/2} \).
With this pressure dependence on momentum, the
pressure independence of \( D t \), the pressure dependence
of \( \lambda \) as \( \lambda_0 (1+bP) \) and \( \nu \) as \( 1/P \), the exponential
behaviour is obtained.

Now, if \( \lambda \nu \propto 1 / P^2 \) and the momentum becomes
directly proportional to applied pressure, and after
expanding the exponential term of Eq. (21), the
desired square power beta density obeyed by the
pyrene-iodine and anthracene-TNB complexes are
obtained.

2.4 Coupling of charge carriers with elastic waves

Consider a physical picture of acousto-electric
domains along one-dimensional conductors, which
easily get perturbed by the application of pressure. It
is considered that there is acoustic attenuation of the
elastic waves, which are coupled with charge carriers
and get dissipated in the system. The dissipation
energy of a semiconductor inherently involves
activation energy or a forbidden energy gap. Both low
and high frequency limits of attenuation coefficients
give rise to different pressure dependence of
resistivity, which corresponds to low frequency
acoustic phonons and high frequency optical phonons.
The acoustic attenuation decays as \( \exp - \gamma \) where \( \gamma \)
is the attenuation coefficient\(^{24} \). The longitudinal and
transverse coefficients are given by:

\[
\gamma_i = \frac{\eta \omega^2}{2 d_c i} = A \omega^2 \quad \ldots (23)
\]
\[ \gamma = \frac{\omega^2}{2 dc_\lambda} \left[ (4/3 \eta + \zeta) + \frac{\kappa \alpha^2}{C_p^2} d^2 \varepsilon_i^2 T \left( 1 - \frac{4c_i^2}{3c_t^2} \right)^2 \right] \]

\[ B = \frac{\pi d^2}{2} \]  

(24)

\[ \eta \text{ and } \zeta \text{ are viscosity parameters, } d \text{ is the mass density, } c_{\lambda \alpha} \text{ are transverse/longitudinal sound velocities. } \alpha \text{ is the thermal expansion coefficient and } \kappa \text{ is the thermal conductivity. The kinetic energy of the elastic wave is given by:} \]

\[ E_k = \frac{1}{2} d \omega^2 (u_{0y}^2 + u_{0z}^2) \]  

(25)

and the dissipation energy is given by:

\[ E_d = \frac{1}{2} 2 \eta \omega^2 (u_{0y}^2 + u_{0z}^2) / c_i^2 \]  

(26)

Now the resistivity \( \rho \) is related to the dissipation energy as:

\[ \rho = 1 / (ne\mu) = \frac{2m^*E_d}{hne^2\nu} \]  

(27)

For the pressure dependence of \( m^* \propto P^2 \), \( E_d \propto \omega^4 \approx (P - P_0)^2 \) as in the case of acoustic phonons and \( \nu \) being independent of pressure due to the formation of a condensate, provides the square beta density behaviour observed in the resistivity measurements.

For the frequencies of the elastic waves in the range \( \chi / a^2 << \omega << c / a \), the attenuation coefficient is given by \( ^{24} \):

\[ \gamma = \frac{T c^2 d c \sqrt{\chi \omega}}{\alpha C} \]  

(28)

where \( \chi \), \( a \), \( c \) and \( C \) are the thermoelectric conductivity, dimensions of the crystallites, velocity of the wave and the specific heat respectively. Considering the concentration of charge carriers according to the Maxwell Boltzmann statistics, \( n = n_0 \exp(-E / K_B T) = n_0(1 - E / K_B T) \) with the energy given in terms of the attenuation coefficient, \( \gamma \) through the damping \( \exp(-2\gamma x) = (1 - 2\gamma x) \) as:

\[ E = \frac{1}{2} d \omega^2 (u_{0y}^2 + u_{0z}^2)(1 - 2\gamma x) \]  

(29)

Using the expression given by Eq. (27) for the resistivity, the half power beta density, \( \rho \propto P^{3/2} (P - P_0)^{1/2} \) is obtained, by considering the pressure variations of the transport parameters as \( \mu \propto P^{1/2} \), \( m^* \text{ and } \nu \text{ not varying with pressure, } \omega \propto (P - P_0) \) and \( \gamma \propto (P - P_0)^{1/2} \).

For polyiodide chain complexes, \( \rho = \frac{K P}{1 + \nu^2} \text{ exp} (E / K_B T) \text{ leads to } \frac{KP}{1 + \nu^2} \text{ exp} - CP \) by considering \( m^* \propto P^2 \), \( \nu \propto P^{1/2} \), \( \lambda = \lambda_0(1 - \alpha P) \), \( \nu \propto P^{3/2} \) and \( E \propto \omega^2 \propto P \). For getting the gaussian dependence, the mobility independent of pressure and \( \omega \propto P \) for optical phonons, must be considered.

### 2.5 Internal reflection of charge density waves

Another mechanism in which the one-dimensional conductors are considered similar in principle to the optical conductivity within optical fibers is discussed here. In the case of one-dimensional conductors, the over-lapping under the external pressure of strongly directional \( p_x \) or \( d_y \) orbitals act as the fiber boundary at which the charge density waves undergo total internal reflection similar to the wave propagation in optical fibers\(^{25-27} \). Application of pressure leads to longitudinal compression and an increase in the fiber diameter due to the Poisson’s ratio. It induces multiple reflections of charge density and or the acoustic waves due to the orbital overlaps. So applying the mechanism of fiber optics, the evanescent modes are considered here at the boundary of the fiber, which is described in terms of the imaginary part of the wave vector\(^{27} \):

\[ \gamma = \omega \sqrt{\mu_0 \varepsilon_z} \sqrt{n_1^2 \sin \theta_1 - 1} \]  

(30)

The charge carriers responsible for the conductivity be proportional to this decay amplitude, i.e \( n \propto \exp - \gamma z \) and \( \gamma \propto \omega \propto P \) for phonons lead to

\[ \rho = \frac{m^* \nu}{ne^2 \nu \lambda} \exp - \gamma z = \frac{KP \exp - CP}{ne^2 \nu \lambda_0(1 - \alpha P)} \]  

(31)

For getting the half power beta density from Eq. (31), the pressure dependence of \( m^* \) as \( P^2 \), \( \nu \propto P^{3/2} \), \( v \propto \lambda \) as independent of pressure, \( \gamma \) small and proportional to \( (P - P_0)^{1/2} \) are required.
For the Gaussian dependence and square power beta density, the $E_2$ of Eq. (30) for $\gamma$ is reconsidered through a damped oscillator model in which:

$$\sqrt{E_2} = \left( \frac{ne^2}{e_0\omega\beta} \right)^{1/2} \left[ 1 - \frac{(\omega_0^2 - \omega^2)}{2(\omega^2 / m^*)^2} \right]$$ \hspace{1cm} \ldots (32)

Now using Eqs. 30-31, a Gaussian dependence is obtained if a strong damping is assumed and $\beta = \omega^2$. For the square power beta density, further it is needed to consider $\beta \approx \omega^2$ through the second order elastic constants. Thus after expanding the exponential part of Eq. (31) gives $\rho \propto P^2 (P - P_0)^2$ as the leading terms.

2.6 Electron-phonon coupling and WKB approximation

The WKB approximation within quantum mechanical description is particularly used when the system is semi classical and macroscopic. This approximation becomes valid when charge density waves or spin density waves are formed as condensates of charge carriers and background lattice vibrations (phonons) through strong electron phonon coupling. In the present study under the external applied pressure the phonon drags the electrons causing an additional potential for the charge carriers and a dependence of electrical resistivity with pressure using the WKB approximation is obtained.

The wave function of a charge carrier under the influence of a potential is given by the WKB approximation as:

$$\psi(x) = AK^{-1/2} \exp \pm \int Kdx$$ \hspace{1cm} \ldots (33)

where $K = \frac{1}{\hbar} [2m^*(E - V))]^{1/2}$. The resistivity is related to the square of the wave function multiplied by the number density, $n$ as:

$$\rho = \frac{1}{en\mu |\psi|^2}$$ \hspace{1cm} \ldots (34)

Under external pressure, $m^* \sim P^2$, $(E - V) \sim (P - P_0)$ and $\mu \sim P^{1/2}$ are assumed. By performing the integration of Eq. (33) in terms of pressure and on substitution in Eq. (34) gives:

$$\rho \propto \frac{1}{ne\mu} P(P - P_0)^{3/2} \exp \{P(P - P_0)^{3/2} - \frac{2}{5}(P - P_0)^{5/2} \}$$ \hspace{1cm} \ldots (35)

Now the half power beta density can be obtained by considering the exponential part as unity which corresponds to the case where the induced potential $V > E$. So for the neutral compounds like DTN and DTN-I$_2$, the external pressure causes an increase in the potential for the charge carriers. While in the case of ionic compounds, like Pyrene-2I$_2$ and anthracene-TNB the exponential term is important and an expansion lead to the square power beta density, where the variation of mobility with pressure becomes small.

2.7 Effect of pressure on fermi level and density of states

Pressure changes the Fermi level and also the density of states indirectly by changing the depth of the traps. Recently this type of changes is considered for explaining the Gaussian or normal (integration of Gaussian curve) distributions observed in optical and infrared spectra of organic conductors. The Gaussian profile may be logarithmically split in the center that can also be encountered on the basis of the density of states given by $D(E) = C |E - E_F|^n$ with $n$ being integer, $C$ a constant. This formulation is utilized for explaining the beta density and exponential relay variations of resistivity in pressure.

The change in Fermi level, $E_F$ under pressure leads to a change in its internal energy, $U$ as:

$$U = \frac{(E - E_F)^2}{n(n + 1)\delta E} \ln D$$ \hspace{1cm} \ldots (36)

and thus band gap reduces to $E_g U$. The resistivity, $\rho$ is now related to the applied pressure through this function. So, under pressure a reduction of band gap occurs according to $E_g \sim E_{g0} - \beta P - U(P)$. For band filling effect $U$ is added and for band tailing $U$ is to be subtracted.

If we consider that the mobility is independent of pressure and do not expand the exponential term, we get Gaussian dependence in pressure using $(E - E_F) \sim (P - P_0)$, where $\ln(E - E_F)$ does not give very pronounced dip due to large background absorption, as found in TMPD – iodine complex.
For $m^*$ independent of pressure $\mu \sim \lambda \nu v \sim P^2$ on the basis of kinetic considerations, leads to $\rho \sim P^2 (P - P_0)^2$ by expanding the exponential term up to second order. The first term has parabolic nature without any peak.

If we consider $\nu \sim (P - P_0)^{3/2}$, $\nu \sim (P - P_0)^{1/2}$ and $\lambda = \lambda_0 (1 - \alpha P)$, leads to the exponential relay dependence of resistivity with pressure.

2.8 Band tailing and $\alpha$-$\sigma$ relation

If the material is disordered, amorphous or inhomogeneous, the width of the band tail is much larger than the thermal energy. Pressure induces elastic energy in the materials and causes deformation potential around a defect or induces additional lattice vibrations like local phonon modes or surface modes. Pressure can also lead to plastic deformation through anharmonic interactions. While, there is sharp end of the energy levels in the forbidden energy gap of anharmonic interactions. While, there is sharp end of the energy levels in the forbidden energy gap of semiconductor and practically there is exponentially falling optical absorption edge. For an ordered or crystalline material, the width of the tail $E_0$ is of the order of a few milli-electron volts and corresponds to a thermal energy which is called an Urbach tail given by:

$$E_0 = \left[ d \ln \alpha \right]^{-1} \quad \ldots \ (37)$$

The band tailing for absorption coefficient is written as:

$$\alpha = \alpha_0 \exp \left( \frac{E - E_1}{E_0} \right) \quad \ldots \ (38)$$

If $\ln \alpha$ vs $h \nu$ is plotted for different compositions then the straight lines near $E_i$ meets at a common point called focal point and the slope gives the determination of the width of the tail. This absorption coefficient $\alpha$ is related to the optical conductivity $\sigma$ as:

$$\sigma = \frac{\alpha n c}{4 \pi} \quad \ldots \ (39)$$

where the real part of the refractive index, $n$, and the velocity of light, $c$, do not change with pressure. Thus using Eqs. (38-39) and substituting energy $(E - E_1)$ of Eq. (38) by the pressure induced vibrational energy as $1/2 k x^2 \sim (P - P_0)^2$ results into the gaussian form for the resistivity with pressure observed in the metal chain dioximes.

Within the second order tight-binding approximation, the force constant, $k$ is proportional to $(P - P_0)^{3/2}$ and the displacement, $x$ proportional to $(P - P_0)$. The refractive index, $n_1$ goes as $1/\nu P$, the half power beta density in pressure for the resistivity will be there if the exponential term up to first order is retained. In the case of ionic complexes that obey the square power beta density in pressure, $n_1$ is proportional to $1/P^2$, and the induced vibrational energy goes as $(P - P_0)^2$, while retaining the first order expansion of the exponential term.

2.9 Hopping conduction of polarons

In the cases of disordered, inhomogeneous and amorphous semiconductors, because of defects, disorders and impurities, the band models are not valid and do not explain the experimental results on such semiconductors. In such cases hopping models and quantum mechanical tunneling models were proposed and employed earlier for organic conductors. In structurally one-dimensional systems, the charge carriers are supposed to move strictly in one dimension, the role of defects, disorders and impurities become very important, so the hopping and percolation models are not out of scope. A situation where the oscillator model mixed with hopping model is considered here, though hopping models do describe the gaussian shape of conductivity in temperature as well as in the small polaron model for the optical properties without using the oscillator model. However, the beta densities in pressure require the use of hopping conductivity and the oscillator model.

The electrical conductivity within hopping model is written as:

$$\sigma = e u_0 n (1 - f) \frac{h W}{k_B T} \quad \ldots \ (40)$$

where, $f = (e^{-\beta E} + 1)^{-1}$ labels the occupation of a site, $u_0 = ea^2 / h$ is a constant having dimension of mobility ($a$ is the lattice constant). The hopping probability, $W$ is given by:

$$W = K \exp \left[ -2 \alpha R_{nn} - E_{nn} / k_B T \right] \quad \ldots \ (41)$$
where \( R_{mm} = R_m - R_m \) and \( E_{mm} = E_m - E_m \) are the position and energy of the two sites, \( \alpha \) is the reciprocal of the Bohr radius of an impurity state. At sufficiently high temperatures the second term in the exponential is small as compared to the first term. So, considering only the \( R_{mm} \) term in the exponential, the resistivity can be written as:

\[
\rho = \frac{K_T}{Ke\nu n(1-f)h} \exp \left( 2\alpha R_0 + 2\alpha \frac{dR}{dt} \tau \right) \quad \ldots (42)
\]

Here, \( R_{mm} = R_0 + \left( \frac{dR}{dt} \right) \tau \) and \( \tau \) is the phonon collision time.

Now by considering the changes \( \frac{dR}{dt} \) is related to the lattice vibration so that, \( \frac{dR}{dt} = \frac{d\omega}{dk} \) which is the group velocity of the acoustic phonon and is given by:

\[
\frac{d\omega}{dk} = \frac{a}{2} (\omega_m^2 - \omega^2)^{1/2} \quad \ldots (43)
\]

By using Eq. (43), Eq. (42) can be reduced to

\[
\rho = \rho_0 \exp \left[ 2\alpha \omega (\omega_m^2 - \omega^2)^{1/2} \right] \quad \ldots (44)
\]

With the pressure variations of the lattice parameter, \( a \sim P \), \( \tau \sim P^{1/2} \) and the usual behaviour of the acoustic phonon frequency \( \omega^2 \sim P \), the shifted half power beta density on expansion of the exponential term is obtained. In the case of acoustic phonon assisted hoping \( \lambda \nu \) remains constant. Only \( \nu \sim P^{1/2} \) for in-phase vibrations by which no collisions occur.

It is also possible to show the square power beta density in pressure if the optical phonon dispersion is considered with some algebraic simplifications based on damped driven oscillator model.\(^{28}\) The parameters \( \lambda \) and \( \nu \) become pressure dependent due to scattering by out-of-phase vibrations of optical phonon modes.

### 2.10 Piezoelectric behaviour in charge transfer complexes

The charge transfer complexes are semiconductors as well as ionic in nature and many ionic conductors are found to be piezoelectric. Both disorder- order and displacive transitions are possible amongst charge transfer complexes. Piezoelectric nature can also arise from plastic or glassy behaviour of these mechanically soft semiconductors.

Here piezoelectric property is considered for the inclusion compounds of iodine and the charge transfer complexes. The theory developed for attenuation of elastic waves or ultrasonic waves is employed in piezoelectric materials. The high-pressure data on the electrical resistivity can be explained through attenuation affecting the dielectric constant of the piezoelectric. This is because electrical resistivity is connected with dielectric constant and pressure effects are related with attenuation of elastic waves. Acousto-electric domains and pressure effects are related with attenuation of elastic waves. Acousto-electric domains which are possible in mechanically soft semiconductors can also lead to modulation and attenuation of pressure generated elastic waves.

The imaginary part of wave vector of the elastic wave in a piezoelectric semi conductor is given by\(^{28}\)

\[
\alpha = \frac{K^2 \omega_0}{2\nu_\gamma} \left[ \frac{1 + \omega_c^2}{\gamma^2 \omega^2} \left( 1 + \frac{2\omega^2}{\omega_c \omega_d} + \frac{\omega^4}{\omega_c^2 \omega_d^2} \right) \right]^{-1} \quad \ldots (45)
\]

Here, \( K \) - the electromechanical coupling constant is defined as \( K^2 = d^2 / e \) with \( e \) as the elastic constant, \( \epsilon \) the dielectric constant and \( d \) as the piezoelectric constant. The parameters \( \omega_0 = \sigma / e \) the reciprocal of the dielectric relaxation time, \( \omega_0 = \nu_s v_d / (fD_n) \) and \( \gamma = 1 + f \nu_d \lambda \nu_s \), where \( f \) is the fraction of the electron concentration due to space charge between the conduction band and the trap states, \( \nu_s \) is the velocity of sound and \( \nu_d \) is the drift velocity of electrons. The electrical resistivity \( \rho \), now will be related to this \( \alpha \) of the above equation as

\[
\rho = \frac{m^* \Delta \xi_{\nu\lambda}}{ne^2 \lambda \nu \Delta \tau} \exp (-\alpha z) \quad \ldots (46)
\]

where \( \Delta \xi \) is the elastic drifts of the charge carriers along the direction of the conducting electrons. Within a first order approximation, and expanding the inverse function of Eq. (45) binomially we can write

\[
\rho = \frac{m^* \Delta \xi_{\nu\lambda}}{ne^2 \lambda \nu \Delta \tau} \frac{d^2}{\varepsilon \varepsilon_c} \left( A - \frac{B}{\omega^2} - C \omega^2 \right) \quad \ldots (47)
\]

Now with the standard description of the pressure dependence of the various transport parameters, the
desired pressure dependence of the resistivity of various complexes discussed in this paper are obtained.

2.11 Tunneling of charge density wave across deformed energy bands

Tunneling of charge density waves (CDW) across the energy bands deformed by the applied pressure is considered. The width of the barrier is narrowed down under the application of pressure. The transmission coefficient of a quantum mechanical potential barrier controls flux of charge carriers having finite momentum. It is similar to the Franz - Keldysh effect in which tunneling of charge carriers occur in the presence of applied electric field. In the present case, instead of the electric field, applied external pressure can induce similar effects. The transmission coefficient for a quantum mechanical potential is given by29:

\[ T = \frac{16E(V_0 - E)}{V_0^2} \exp(-2\beta a) \]  \hspace{1cm} (48)

where \( \beta = \frac{1}{\hbar} \left(2m(E-V_0)\right)^{1/2} \) and \( V_0 \) and \( a \) are the height and width of the potential barrier. Under the external pressure \( P \), we assume that \( V_0 - E \propto P \), and that \( \lambda \) is limited to the wave length of the CDW which is pressure independent. Then, \( m^* \sim \Delta E \sim V_0 - E \) and \( m/m^* = 1 + (\hbar^2/2ma^2)/\Delta E \) as per the degenerate perturbation theory.30. Now, the mobility of the charge carrier, \( \mu \sim p \) leads to the pressure dependence of the electrical resistivity of the inclusion compounds of iodine.

The mobility \( \mu \) goes as:

\[ \mu = \frac{m^* v}{e\lambda v} = C \frac{\tau P}{e\lambda P^{3/2}} \approx P^{1/2} \]  \hspace{1cm} (49)

where, \( \tau \), \( \lambda \), and \( A \) (area) are independent of pressure. Using \( m^* \sim V_0 E \) and expanding exponential to first order leads to the half power beta density relation of the resistivity in pressure. The square power beta density dependence can be obtained using \( m^* \sim V_0 E \), and relating the transmission coefficient \( T \) of Eq. (48) directly with the electrical conductivity \( (\sigma) \) along with the relationship of the activation energy \( E_a \sim E^0_0 - \gamma P \), that appear in the carrier concentration(\(n\)) and expanding the exponential term up to the first order.

All the theoretical models discussed above are summarized in Tables 1-4 to high light the dependence of the various transport parameters of the different low dimensional conductors studied in this paper.

<table>
<thead>
<tr>
<th>Table 1—Relay function satisfied by inclusion compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenomenology based on different physical mechanisms</td>
</tr>
<tr>
<td>Classical treatment</td>
</tr>
<tr>
<td>Energy fluctuation in canonical Ensemble</td>
</tr>
<tr>
<td>Diffusion processes</td>
</tr>
<tr>
<td>Elastic Waves</td>
</tr>
<tr>
<td>Internal Reflection of CDWS</td>
</tr>
<tr>
<td>Density of States</td>
</tr>
<tr>
<td>Barrier Tunneling</td>
</tr>
<tr>
<td>Piezoelectric model</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2—Square power beta density of ionic charge transfer complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenomenology based on different physical mechanisms</td>
</tr>
<tr>
<td>Classical treatment</td>
</tr>
<tr>
<td>Energy fluctuation in canonical Ensemble</td>
</tr>
<tr>
<td>Diffusion processes</td>
</tr>
<tr>
<td>Elastic Waves</td>
</tr>
<tr>
<td>Internal Reflection of CDWS</td>
</tr>
<tr>
<td>Density of States</td>
</tr>
<tr>
<td>Barrier Tunneling</td>
</tr>
<tr>
<td>Piezoelectric model</td>
</tr>
<tr>
<td>Hoping Conduction</td>
</tr>
</tbody>
</table>
The four distinct experimental behaviours of the resistivity, $\rho \sim P^{1/2}$ ($P_0P$)$^{1/2}$, the half power beta density behaviour for neutral charge transfer complexes; $\rho \sim P^2$ ($P_0P$)$^2$, the square power beta density behaviour for ionic charge transfer complexes; $\rho = (KP/I+Bp)e^{CP}$ the relay function for organometallic conductors under high pressure have been analyzed based on various physical processes that could happen within such materials under the application of pressure. The different transport parameters of each compound / complex and their dependence on the external applied pressure have been deduced. The basic dependence of the resistivity with the transport parameters of semiconductors is employed in present analysis. The phenomenological models are to be related to the kinetic theories and other microscopic quantum models. Various physical mechanisms that regulate the transport parameters to yield the experimental behaviour of the resistivity of the compounds are presented in Tables 1-4. The pressure dependence of the various transport parameters is important both in its physics point of view as well as for its applications.

The pressure dependencies of the transport parameters through various physical mechanisms described in this paper do reveal the consistencies and deeper connections among the basic material properties. These theories can also be applied to metals, semiconductors and ionic materials in which similar pressure behaviour of resistivity is observed. The different pressure dependence of the various transport parameters deduced for each case discussed in this paper reveal the interdependence of the phenomenology with the basic theory. For example, $m^* \sim \text{const}$ can be according to the tight binding model of solids, $m^* \sim P^2$ or $(P-P_0)^{3/2}$ corresponds to degenerate perturbation theory and coupled bands in solids. Similarly, the parameters such as $\lambda = \lambda_d(1-\alpha P)$, $v \sim P^{3/2}$ or $(P-P_0)^{3/2}$, $\omega \sim P^{1/2}$ or $(P-P_0)^{3/2}$ are according to kinetic theory of free charge carriers, while $\omega \sim P^{1/2}$ corresponds to excitations of the acoustic phonons and $\omega \sim P$ corresponds to that due to optical phonons. However, there are few cases where one requires new physical insights to explain the respective pressure dependence of the transport parameters.

### Table 3—Half power beta density of neutral charge transfer complexes

| Classical treatment | Using | $m^* \sim (P-P_0)^{3/2}$; $v \sim P^{1/2}$ 
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann Distribution</td>
<td>$\rho \sim P-P_0$</td>
<td>$\frac{\partial n}{\partial v} \sim P-P_0$</td>
</tr>
<tr>
<td>Energy fluctuation model</td>
<td>$n v \sim P^{3/2}$ or $(P-P_0)^{3/2}$</td>
<td>$m^* \sim \text{const} ; \gamma \sim (P-P_0)^{3/2}$</td>
</tr>
<tr>
<td>Elastic Waves</td>
<td>$\lambda \sim \text{const} ; \mu \sim P^{1/2}$; $\omega \sim (P-P_0)$</td>
<td></td>
</tr>
<tr>
<td>Internal Reflection of CDWS</td>
<td>$m^* \sim P^3$; $v \sim P^{3/2}$; $\gamma \sim (P-P_0)^{3/2}$</td>
<td></td>
</tr>
<tr>
<td>Band Tailing</td>
<td>$k x^3 \sim (P-P_0)^{3/2}$; $n_t \sim P^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>Piezoelectric model</td>
<td>$m^* \sim P^{3/2}$; $\beta \sim a^3 \sim P$</td>
<td></td>
</tr>
<tr>
<td>Hoping Conduction</td>
<td>$\omega \sim P^{3/2}$; $\lambda v \sim \text{const}$; $\tau \sim P^{1/2}$; $a \sim P$</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4—Gaussian function of organo-metallic conductors

<table>
<thead>
<tr>
<th>Classical treatment</th>
<th>Using</th>
<th>$m^* \sim (P-P_0)^3/2$; $v$, $\mu$, $\lambda$, $\omega$ ~ constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann Distribution</td>
<td>$\rho \sim P-P_0$</td>
<td>$\rho \sim P-P_0$</td>
</tr>
<tr>
<td>Energy fluctuation in canonical Ensemble</td>
<td>$E-U-(P-P_0)$; Other parameters as pressure independent.</td>
<td></td>
</tr>
<tr>
<td>Diffusion processes</td>
<td>$\lambda / P \sim \text{const} ; Dt \sim \text{const}$</td>
<td></td>
</tr>
<tr>
<td>Elastic Waves</td>
<td>$\mu \sim \text{const} ; \omega \sim P$</td>
<td></td>
</tr>
<tr>
<td>Density of States</td>
<td>$\mu \sim \text{const} ; E_k \sim E_{k_0} - \beta P^\pm U(P)$</td>
<td></td>
</tr>
<tr>
<td>Band tailing</td>
<td>$n_t \sim \text{const} ; E - E_1 \sim P$; $k x^3 \sim (P-P_0)^3/2$</td>
<td></td>
</tr>
</tbody>
</table>

### References