PREFACE

This thesis deals with solid state spectroscopy of charge transfer complexes of magnetic conductors, organic ferromagnets and their precursors. Here we work with electron – donor or as electron acceptors.

In this chapter we studied details of charge transfer complexes, Peierls transition, charge ordering, spin-Peierls, spin-density wave, antiferromagnetic state, superconductivity, charge-density wave and electrical conductivity.

We studied One and Two dimensional conductors, Mott transition, delocalization, Kohn anomaly and Peierls instability, Organic ferro-magnetism, forbidden direct transition gaussian band and Hubbard model.

We also studied the necessary condition for the occurrence of hopping, absorption of radiation by semiconductors, allowed indirect transition, forbidden direct transition, indirect transition and free – carrier absorption.

Organic conductors consist of donor and acceptor molecules building separated planar sheets or columns. The energy difference in the ionization energy of donor and the electron affinity of the acceptor leads to a charge transfer and consequently to free carriers whose number is normally fixed. The carriers are delocalized throughout the crystal due to the overlap of the molecular orbitals being also reasonable for the high

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anisotropic conductivity. That is why it will be distinct between different dimensional organic conductors. They possess a huge variety of ground states, for instance, charge ordering, spin-Peierls, spin-density wave, antiferromagnetic state, superconductivity, charge-density wave to name only some of them.

In **chapter 2** the Fourier – transform infrared spectra of complexes of TEMPO free radical with organic acceptors such as TCNQ, TCNE, DDQ, chloranil, iodine have been studied. Some of them have ferro or antiferromagnetic properties at very low temperatures. From FTIR spectra, these complexes are found to be small band-gap semiconductors. They are interpreted as Hubbard semiconductors having non-universal band gap. They also show either asymmetric or symmetric Gaussian band revealing electronic delocalization. They are expected to be paramagnetic.

In **chapter 3** the FTIR spectra of charge transfer complexes of galvinoxyl with organic acceptors such as TCNQ, TCNE, DDQ, chloranil and iodine have been studied in the present work. This study has been carried out in the mid – IR range, i.e. 400 – 4000 cm\(^{-1}\). Above 1600 cm\(^{-1}\), a half power beta density in absorption is observed revealing hopping conduction in these CT complexes. The nature of transition is analyzed below 1600 cm\(^{-1}\) showing a very small band gap of 0.02 – 0.05 eV. This small band gap is associated with CDW or SDW pinning gap. The band gap can be covered by large band tailing or addition shrinkage due to electron – electron interaction. Electrically the CT complexes are paramagnetic at room temperature. The transition to diamagnetic state of galvinoxyl can be suppressed at low temperatures because of charge transfer.
In chapter 4 the present study the FTIR spectra of some \((\text{TMTSF})_2X\) type charge transfer complexes where \(X\) is an electron acceptor are investigated. It is found that these are ionic complexes with half – an electron transferring from each of TMTSF donor molecule. There are dimmers of donor molecules which are positively charged and acceptor molecules which are negatively charged. The complexes contain \(\text{TCNQ}^-\), \(\text{semiquinone}^-\), \(\text{TCNE}^-\), \(\text{Chloranil}^-\) and \(\text{I}_3^-\) ions. These are similar to \((\text{TMTTF})_2X\) and \((\text{TMTSF})_2X\) type complexes in which superconductivity is found at low temperatures.

In chapter 5 the FTIR spectra of meso – tetraphenylporphine (TPP) and its charge transfer complexes with standard organic acceptors have been obtained. The spectrum of TPP shows a half – power beta density in absorption, a Lorentzian in the mid – IR range and a low – frequency gaussian band. TPP – TCNQ, TPP – TCNE and TPP – Chloranil show \(\alpha =\) constant above 1800 cm\(^{-1}\), revealing two – dimensional nature of the materials. TPP – TCNQ and TPP – \(\text{I}_2\) show a gaussian band between 1000 cm\(^{-1}\) and 1700 cm\(^{-1}\) associated with delocalization of charge carriers. Below 1000 cm\(^{-1}\), all CTCS of TPP show a Lorentzian curve at low frequency. TPP – DDQ, TPP – Chloranil and TPP – \(\text{I}_2\) show a range of nature of transition which is analyzed as direct transition. TPP – DDQ shows a two – band transport.

In chapter 6 the present work the charge transfer complexes of TDAE – tetrakis(dimethylamino)ethylene which is a precursor of organic ferromagnet such as \((\text{TDAE}) – \text{C}_60\). CTCS of TDAE with standard organic acceptors are studied. TDAE is found form CTCS with TCNQ, TCNE, DDQ, chloranil and iodine. It is found to that most of them are indirect band gap
semiconductors and two dimensional. The indirect interband transition is explained with macromolecular nature of TDAE. Macromolecules furnish phonons required in indirect transition due to their mechanical flexibility. Thus TDAE behaves similarly as many macromolecular bimolecules.

In chapter 7 Decamethylferrocene (DMF) and its charge transfer complexes with standard organics TCNQ, TCNE, DDQ, Chloranil and iodine have been studied using FTIR spectroscopy in the present work. Decamethylferrocene having Fe$^{+2}$ ion is a semiconductor. TCNQ and TCNE complexes show two – dimensional behavior. DDQ and chloranil complexes show a one – dimensional semiconducting behavior with direct transition. Iodine complex shows a range of free – carrier absorption due to the scattering by acoustic phonons. Almost all complexes show oscillations in the density of states.

In chapter 8 the charge transfer complexes of bis(pentamethylcyclodienyl) Co$^{II}$ and bis(pentamethylcyclodienyl) Co$^{III}$ PF$_6$ with standard organic acceptors are prepared and FTIR spectra are obtained and studied in the present work. Co$^{II}$ compound shows a direct transition, a half – power beta density and an asymmetric gaussian band in IR spectrum. Its TCNQ and TCNE complexes show similar spectra. Its DDQ, Chloranil and Iodine complexes show imperfect nesting of Fermi surface. Co$^{III}$ compound show two dimensional conductivity which is retained in its TCNQ, TCNE and DDQ complexes while chloranil and iodine complexes reveal semi metallic behavior.
In chapter 9 the well-known luminescent material 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) works as an electron donor due to four phenyl rings and forms charge transfer complexes with acceptors such as TCNQ, TCNE, DDQ, Chloranil and iodine. The FTIR spectra of these CTCS are studied in the present work. The spectrum of TPB contains a beta density in absorption due to hopping conduction. TCNQ, TCNE and iodine complexes shows a broad and pronounced peak in mid-IR range corresponding to a maximum in optical conductivity. DDQ complex. shows a gaussian band below mid-IR range. Chloranil complex. shows an allowed direct interband transition and oscillation in the density of states.

In chapter 10 the FTIR spectra of charge transfer complexes of the type (BEDT – TTF) X has been investigated, where X is a standard organic acceptor. TCNQ, TCNE, DDQ, Chloranil and iodine have been tried as acceptors. TCNQ and iodine are found to enhance hopping conduction occurring in BEDT – TTF. TCNE, DDQ and Chloranil complexes lead to semiconducting behavior with optical absorption edge lying in the infrared range. The analysis shows that these CTCS are having direct transition from valance to conduction band.