CHAPTER 6
ELECTRICAL AND MAGNETIC STUDY OF CRYSTAL

6.1 INTRODUCTION

In order to study the electrical properties, the ideal contact to the semiconductor would be the one which satisfies the following properties.

- No resistance to the flow of the current is induced
- Does not react chemically with the semiconducting material
- Contact properties are not affected by variation of illumination, temperature, electrical field or any other ambient conditions, and
- The semiconductor with contacts applied should satisfy ohms law.

The existence of barriers is usually observed when a contact is made between a metal and a semiconductor because of either improper matching of the work functions between the metal and semiconductor or the presence of surface states on the semiconductor or the presence of a thin layer of oxides. A contact between a metal and a semiconductor will be proper when no such barriers exist such a contact is generally known as “ohmic contact”.

The silver paste either cold or hot gives good contacts as is observed in most of the organic semiconducting materials. Leads of 46 swg copper wires were soldered directly to the silver deposit.

The nature of the contacts was checked by measuring the current-voltage characteristics for all the samples.
6.1.1 Current-Voltage measurements:

The various current-voltage characteristics were measured for all samples in order to ascertain the nature of the current transport. The details of the method are described below.

[A] AC Method:

The sample in series with a variable resistance (0-3 X 10^6 ohms) was connected to a triangular function generator as shown in figure 4.1.

![Circuit diagram for the determination of I-V Characteristics](image)

Figure 6.1 - Circuit diagram for the determination of I-V Characteristics

The voltage drop across the resistance “R” was fed to the Y-amplifier of the oscilloscope (Tektronix 515 A). The X- and Y- gain of the amplifiers was adjusted so as to limit the trace of the beam within the view of the oscilloscope and was calibrated with the internal calibration signal. As the voltage drop across “R” was equal to RI (Where R is the resistance and I the current). The
beam directly traced the current-voltage characteristic of the sample which was photographed for further analysis.

The range of triangular voltage $V$ and its repetition frequency was controlled by the control panel of the generator which had an output impedance of 600 ohms and was capable of delivering a maximum current of 12 mA at 100 volts with least 1% distortion. If the general is loaded output voltage falls but still the I-V characteristic of the sample remains unaffected. However for excessive loading the same begins to behave as a constant current generator and current controlled properties of a device can be studied.

[B] DC Method:

![Schematic circuit diagram for I-V characteristics by DC method](image)

Where, $S$ = Sample, $P$ = Variable power supply, $V$ = Voltmeter, $A$ = Electrometer

**Figure 6.2 - Schematic circuit diagram for I-V characteristics by DC method**

A rectangular sample having silver electrode is connected in series with a sensitive electrometer, a standard resistor (1 meg.) and a variable power
source as shown in the figure 4.2. The voltage drop across the sample and resistor was measured with DC micro voltmeters (Philips). The current voltage characteristic was noted by changing the potential difference across the sample. Sufficient time was allowed, after the change of voltage to get the steady values of current. The characteristics were noted for both +Ve and –Ve value of voltages at room temperature. The voltage drop across the resistor was in order to check the current measured from the electrometer.

### 6.1.2 DC Electrical resistivity measurements: (300-500 °K)

For high resistivity materials ($\rho_{RT} > 10^4$ ohm. cm.) ASTM [1] has recommended the two probe method to be the most accurate one. The resistance of the materials was measured by using “Hewlett Packard 4329 A high resistance meter” in which a known voltage passed through the ends of the samples and the corresponding resistance was read directly. In the present experiments, the electrical conductivity of samples were measured in the form of pellets and prepared as follows [2]:

The sample were crushed into a fine powder and passed into cylindrical pellets under hydrostatic pressure (1 X $10^4$ lbs / inch$^2$). The samples thus obtained were hard and crack-free (at least to the necked eye). A thin layer of Ag-paste was applied on both the slides and cured at 50°C for 2 hrs. (As prescribed by the manufacturer), which acted as the electrodes. The pellets were of 2.88 cm in diameter and 2-3 in thickness.

The sample holder assembly and the furnace used in the experiment. The sample pellet was pressed firmly between two circular brass electrodes. brass discs of 15 mm diameter and cleaned before every experiment. The other end of the electrodes were passed through the Teflon blocks of 2 X 2’ and taken out for connections. The entire assembly was covered with aluminum, which was earthed and placed at the centre of a tubular furnace. The
temperature of the furnace could be maintained to within ± 0.5-1°C of the desired temperature by means of a dimmer stat. A pre calibrated chromelalumel thermocouple placed very near the sample (~ 1 mm) was used to measure the sample temperature. The sample temperature (i.e., thermocouple e.m.f.) was measured by using of slide wire potentiometer using external galvanometer.

Both heating and cooling runs were taken in order to check any thermal hysteresis effect present.

Resistivity (ρ) is calculated using the equation

\[ \rho = R_r \frac{A}{l} \]  

(6.1)

where, \( R_r \) = resistance,
\( A \) = cross sectional area of the sample normal to the voltage
\( l \) = distance between the two electrodes.

The value of electrical conductivities of the crystal sample prepared under different experimental conditions and the chelates of the crystal sample. Thus the measurements are made at temperatures ranging from 35°C to 270°C. It was indicated earlier that the conductivity of semiconducting material is related to temperature exponentially \(^3\).

\[ \sigma = \sigma_0 \exp (-E/KT) \]  

(6.2)

Where, \( K = \) Boltzmann constant (0.8625 x 10\(^{-4}\) ev deg\(^{-1}\))
\( T = \) absolute temperature
\( \sigma_0 = \) Conductivity at infinite temperature,
\( E = \) activation energy.

The relation is relation is written in a different form as follows:
According to the relation, plot of log\(\sigma\) vs. 1/T would be linear with a negative slope. Such plots were made on the basis of each set of data. The influence of charges is characterized in terms of the forces between them (Coulomb's law) and the electric field and voltage produced by them. One Coulomb of charge is the charge which would flow through a 120 watt lightbulb (120 volts AC) in one second. Two charges of one Coulomb each separated by a meter would repel each other with a force of about a million tons! The rate of flow of electric charge is called electric current and is measured in Amperes. In introducing one of the fundamental properties of matter, it is perhaps appropriate to point out that we use simplified sketches and constructs to introduce concepts, and there is inevitably much more to the story. No significance should be attached to the circles representing the proton and electron, in the sense of implying a relative size, or even that they are hard sphere objects, although that's a useful first construct. The most important opening idea, electrically, is that they have a property called "charge" which is the same size, but opposite in polarity for the proton and electron. The proton has 1836 times the mass of the electron, but exactly the same size charge, only positive rather than negative. Even the terms "positive" and "negative" are arbitrary, but well-entrenched historical labels. The essential implication of that is that the proton and electron will strongly attract each other, the historical archetype of the cliché "opposites attract". Two protons or two electrons would strongly repel each other. Once you have established those basic ideas about electricity, "like charges repel and unlike charges attract", then you have the foundation for electricity and can build from there.

From the precise electrical neutrality of bulk matter as well as from detailed microscopic experiments, we know that the proton and electron have the same magnitude of charge. All charges observed in nature are multiples of
these fundamental charges. Although the standard model of the proton depicts it as being made up of fractionally charged particles called quarks, those fractional charges are not observed in isolation -- always in combinations which produce +/- the electron charge.

An isolated single charge can be called an "electric monopole". Equal positive and negative charges placed close to each other constitute an electric dipole. Two oppositely directed dipoles close to each other are called an electric quadru pole. You can continue this process to any number of poles, but dipoles and quadru poles are mentioned here because they find significant application in physical phenomena.

One of the fundamental symmetries of nature is the conservation of electric charge. No known physical process produces a net change in electric charge

Electric current is the rate of charge flow past a given point in an electric circuit, measured in Coulombs/second which is named Amperes. In most DC electric circuits, it can be assumed that the resistance to current flow is a constant so that the current in the circuit is related to voltage and resistance by Ohm's law. The standard abbreviations for the units are 1 A = 1C/s.

Electrical conductivity is the ability of a material to carry the flow of an electric current (a flow of electrons). Imagine that you attach the two ends of a battery to a bar of iron and a galvanometer. (A galvanometer is an instrument for measuring the flow of electric current.) When this connection is made, the galvanometer shows that electric current is flowing through the iron bar. The iron bar can be said to be a conductor of electric current. Replacing the iron bar in this system with other materials produces different galvanometer readings. Other metals also conduct an electric current, but to different extents. If a bar of silver or aluminum is used, the galvanometer shows a greater flow of electrical current than with the iron bar. Silver and aluminum are better conductors of electricity than is iron. If a lead bar is inserted, the galvanometer shows a lower
reading than with iron. Lead is a poorer conductor of electricity than are silver, aluminum, or iron.

Many materials can be substituted for the original iron bar that will produce a zero reading on the galvanometer. These materials do not permit the flow of electric current at all. They are said to be nonconductors, or insulators. Wood, paper, and most plastics are common examples of insulators. Another way of describing the conductivity of a material is through resistance. Resistance can be defined as the extent to which a material prevents the flow of electricity. Silver, aluminum, iron and other metals have a low resistance (and a high conductivity). Wood, paper, and most plastics have a high resistance (and a low conductivity). The unit of measurement for electrical resistance is called the ohm (abbreviation: Ω). The ohm was named for German physicist Georg Simon Ohm (1789–1854), who first expressed the mathematical laws of electrical conductance and resistance in detail. Interestingly enough, the unit of electrical conductance is called the mho (ohm written backwards). This choice of units clearly illustrates the reciprocal (opposite) relationship between electrical resistance and conductivity. Electrical conductivity occurs because of the ease with which electrons can be removed from atoms. All substances consist of atoms. In turn, all atoms consist of two main parts: a positively charged nucleus and one or more negatively charged electrons. An atom of iron, for example, consists of a nucleus with 26 positive charges and 26 negatively charged electrons.

The electrons in an atom are not all held with equal strength. Electrons close to the nucleus are strongly attracted by the positive charge of the nucleus and are removed from the atom only with great difficulty. Electrons farthest from the nucleus are held only loosely and are removed quite easily. A block of iron can be thought of as a huge collection of iron atoms. Most of the electrons in these atoms are held tightly by the iron nuclei. But a few electrons are held loosely—so loosely that they act as if they don't even belong to atoms at all. Scientists sometimes refer to this condition as a cloud of electrons. Normally these "free" electrons have no place to go. They just spin around randomly among the iron atoms. That situation changes, however, when a battery (or other source of electric current) is attached to the iron block. Electrons flow out
of one end of the battery and into the other. At the electron-rich end of the battery, electrons flow into the piece of iron, pushing iron electrons ahead of them. Since all electrons have the same negative charge, they repel each other. Iron electrons are pushed away from the electron-rich end of the battery towards the electron-poor end. In other words, an electric current flows through the iron. Insulators have a very different structure. They too consist of atoms (nuclei and electrons), but very few free electrons can be found in insulators. Those electrons tend to be bound tightly to nuclei in chemical bonds. Attaching a battery to an insulator has no effect since there are no free electrons to be pushed through the material. Electrons are not the only particles capable of carrying an electric current. Ions can do it, too. An ion is an atom or group of atoms with an electric charge. Suppose you dissolve a crystal of table salt (sodium chloride) in water. Salt crystals consist of positive sodium ions and negative chloride ions. In the solid state, these ions are not free to move around. Once they are dissolved in water, however, they become completely mobile. They are free to "swim" about in the water and to respond to an electric current from a battery. That current supplies electrons that cause positive sodium ions to flow in one direction and negative chloride ions to flow in the opposite direction.

A good example of this effect can be seen in the conductivity of water. Pure water consists only of water molecules. The electrons in water molecules are held tightly by hydrogen and oxygen atoms and are not free to move. Attaching a battery to a container of water produces no electric current because pure water is an insulator. But a few grains of table salt added to the water changes things completely. Sodium ions and chloride ions are released from the salt, and the salt water solution becomes conductive. Some materials cannot be classified as either conductors or insulators. Semiconductors, for example, are materials that conduct an electric current but do so very poorly. Semiconductors were not well understood until the mid-twentieth century, when a series of remarkable discoveries revolutionized the field of electrical conductivity. These discoveries have made possible a virtually limitless variety of electronic devices, ranging from miniature radios and handheld calculators to massive solar power arrays and orbiting telescopes. Superconductivity is a property that appears only at very low temperatures, usually close to absolute
zero (−273°C). At such temperatures, certain materials lose all resistance to electric current; they become perfect conductors. Once an electric current is initiated in such materials, it continues to flow without diminishing and can go on essentially forever. The discovery of superconductivity holds enormous potential for the development of electric appliances. In such appliances, a large fraction of the electrical energy supplied to the device is lost in overcoming electrical resistance within the device. That lost energy shows up as waste heat. If the same appliance were made of a superconducting material, no energy would be lost because there would be no resistance to overcome. The appliance would become, at least in principle, 100 percent efficient.

Many attempts have been made to synthesize new materials which can be used as semiconductors \(^{[1,2]}\). Some of the organic compounds do show good conductivity, photo conductivity etc. \(^{[3,4]}\). The band gap and the conductivity of such compound should fall within the required range and should be also easy to prepare. The main drawback of organic compounds is low carrier mobility. The reasons for this are:

A) Organic compounds form molecular crystals and the forces between the adjacent molecules are relatively weak. There is ultimately little electrical coupling between adjacent molecule and thus electrons find it difficult to jump from one molecules to another.

b) Many of these are amorphous in nature. The lack of ordered structure in such materials has the effect of scattering electrons when they try to flow through it and hence lowers the conductivity.

It is feasible to overcome the above difficulties by making suitable coordination polymers of transition metals. Using aromatic ligands and bridging them by metal atoms through conjugation it is possible in the above compounds, i.e. metal d-orbital to form \(\pi-\pi\) bonds to the adjacent ligands. Next, the linkage of organic molecules to each other by metal-metal bonds would be
expected to increase greatly the ease of intermolecular migration of electrons and hence the carrier mobility.

As mentioned earlier, the wide applicability of polymers encourage the research workers to explore this field. Since the last two and a half decades, voluminous literature has appeared in this field. The electrical properties of this class of polymers are reviewed briefly. Kunda et al \[4\] prepared the copper derivatives of 2,5-dihydroxy quinine and its chloro and bromo substituents. They have also prepared Cu(II), Ni(II) and Cd(II) polymers from 2,5-dihydroxy benzophenone. The resistivity of the Cu(II) derivative were measured but no reproducible results were got. Terentev et al \[5\] have prepared the polychelates from the poly(Schiff base) obtained from the condensation of 5,5’-methylene bis salicylaldehyde and o-phenylene diamine, hexamethylene diamine and ethylene diamine. The polychelate from hexamethylene diamine showed enhanced conductivity which was attributed to the close packing and better intra molecular contact between the conjugated sectors of the macromolecules. Korshak et al \[6\] reported copper (II) poly phenyl acetylide which was formed by the action of ammonical copper (II) nitrate on p-diethylaryl benzene in alcohol. An ESR study of these polymers showed spin concentration of up to $10^{19} / g$ the very narrow signals and absence of hyperfine structure indicating a high degree of electron delocalization in the conjugated chain. Kunda et al \[7\] measured the AC and DC electrical conductivities of quinine type copper derivatives. The quinine type copper polymers gave no reproducible values of resistivity either with DC or AC measurements. Vozzhenikov et al \[8\] presented the new data on the electrical conductivity and energy of activation of dithioxamide, N-substituted dithiocarbamate and dithiocyanate Cu, Ni, Co polymers. Terentev et al \[9\] have prepared the cross linked polymer by reaction of 2,6-diacetyl pyridine with o-phenylene diamine, hexamethylene diamine and metal salts. Parini et al \[10\] prepared polymeric ligands containing an occasional azo group between the quinine and aromatic residues by reacting p-benzoquinone with the bis azocompounds prepared from p-phenylene diamine,
benzidine-3,3’-dicarboxylic acid. The products were semiconducting and reacted with heavy metal salts to produce cross linked polymers, the resistivity of which however is not reported. Zhang and Yu Li studied electrical conductivity of polyaniline\(^{[11]}\). Cabajal \(^{[12]}\) investigated the electrical properties of squaric acid-Cu (II) polymer. This was prepared by solid solid reaction between copper acetonate or CuCl\(_2\).2H\(_2\)O and squaric acid, melt reaction of squaric acid and copper salts. Manecke et al \(^{[13]}\) reported the semiconducting properties of polymeric Schiff bases including polychelate of 2,5-dihydroxy terephthalaldehyde and a series of di- and tetraamine compounds and diaminodihydroxy compounds. Talati et al \(^{[14]}\) have prepared some poly chelates of hydroxyl quinones and studied their electrical properties. They are correlated the band gap with the number of \(\pi\)–bonds present in the ligand.

The magnetic moment of a magnet is a quantity that determines the force the magnet can exert on electric currents and the torque that a magnetic field will exert on it. A loop of electric current, a bar magnet, an electron, a molecule, and a planet all have magnetic moments\(^{[15-18]}\). Both the magnetic moment and magnetic field may be considered to be vectors having a magnitude and direction. The direction of the magnetic moment points from the south to north pole of a magnet. The magnetic field produced by a magnet is proportional to its magnetic moment as well. More precisely, the term *magnetic moment* normally refers to a system's magnetic dipole moment, which produces the first term in the multipole expansion of a general magnetic field. The dipole component of an object's magnetic field is symmetric about the direction of its magnetic dipole moment, and decreases as the inverse cube of the distance from the object. The sources of magnetic moments in materials can be represented by poles in analogy to electrostatics. Consider a bar magnet which has magnetic poles of equal magnitude but opposite polarity. Each pole is the source of magnetic force which weakens with distance. Since magnetic poles always come in pairs, their forces partially cancel each other because while one pole pulls, the other repels. This cancellation is greatest when the poles are
close to each other i.e. when the bar magnet is short. The magnetic force produced by a bar magnet, at a given point in space, therefore depends on two factors: on both the strength \( p \) of its poles, and on the vector separating them. The analogy with electric dipoles cannot be taken too far. Magnetic dipoles are associated with angular momentum, as demonstrated by the Einstein-de Haas effect and the Barnett effect, for example. Therefore, they do not behave like ideal magnetic dipoles. In particular, although a magnetic dipole is subject to a torque in a magnetic field that tends to align its magnetic moment with the applied magnetic field, as a consequence of the associated angular momentum, the magnetic dipole processes, that is, its direction rotates about the axis of the applied field. Nevertheless, magnetic poles are very useful for magneto static calculations in ferromagnetism\(^{[19-21]}\). Suppose a planar closed loop carries an electric current \( I \) and has vector area (\( x \), \( y \), and \( z \) coordinates of this vector are the areas of projections of the loop onto the \( yz \), \( zx \), and \( xy \) planes). Its magnetic moment, vector, is defined as:

By convention, the direction of the vector area is given by the right hand grip rule (curling the fingers of one's right hand in the direction of the current around the loop, when the palm of the hand is "touching" the loop's outer edge, and the straight thumb indicates the direction of the vector area and thus of the magnetic moment)\(^{[22-26]}\). In electromagnetism, the magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field. The intensity of magnetization, \( I \), is related to the strength of the inducing magnetic field, \( H \), through a constant of proportionality, known as the magnetic susceptibility. The magnetic susceptibility is a unit less constant that is determined by the physical properties of the magnetic material. It can take on either positive or negative values. Positive values imply that the induced magnetic field, \( I \), is in the same direction as the inducing field, \( H \). Negative values imply that the induced magnetic field is in the opposite direction as the inducing field\(^{[27-29]}\).

\[
I = KH
\] (6.4)
In magnetic prospecting, the susceptibility is the fundamental material property whose spatial distribution we are attempting to determine. In this sense, magnetic susceptibility is analogous to density in gravity surveying.

6.2 MAGNETIC SUSCEPTIBILITY STUDY

The magnetic properties have been used in inorganic chemistry mainly to investigate valence and stereo chemical aspects of crystals. This magnetochemical method of study has gained special significance since the development of quantum mechanical theory of coordination compounds by Pauling. In inorganic chemistry, hence measurements are useful for three main purposes, provided the number of unpaired electrons can be deduced from the magnetic moment. It is possible to infer\textsuperscript{31-32}

(i) The valency
(ii) The bond type and
(iii) Stereo chemical arrangement of the bonds around a particular atom.

The magnetic field inside the substance differs from the free space value of the applied field. The difference can be put in the form\textsuperscript{33}.

\[
H = Ho + H1 \tag{6.5}
\]

Where, \( H \) = magnetic induction, \( Ho \) = free space magnetic field, \( H1 \) = the field produced by magnetic polarization of the substance.

The magnetic induction (B) or the density of lines of forces within the substance in the presence of magnetic field is given by

\[
B = Ho + 4\pi I \tag{6.6}
\]

Where ‘I’ is intensity of magnetic moment per unit volume. On dividing the last expression by \( Ho \) we get

\[
B/Ho = 1 + 4\pi K \tag{6.7}
\]

\( B/Ho \) is referred as magnetic permeability of the substance. K is magnetic susceptibility per unit volume of the substance.
The molar susceptibility $\chi_M$ is obtained by multiplying a gram susceptibility $\chi_g$ by molecular weight.

$$\chi_M = \chi_g \times \text{molecular weight} \quad (6.8)$$

6.2.2 Types of magnetic behavior

(i) Diamagnetism

When permeability is less than one, diamagnetism arises. For the diamagnetic substance, values of I, K and $\chi$ are negative. Diamagnetism causes the reduction in the density of lines of forces i.e. when substance placed in non homogeneous magnetic field, it will tend to move to the region of the lowest field strength. The value of $\chi$ is negative and independent of temperature and field strengths.

(ii) Paramagnetism

When permeability is greater than one, paramagnetism arises. Here I, K and $\chi$ are positive. Paramagnetism increases the density of lines of forces, i.e. when substance is placed in non homogeneous magnetic field, it will tend to move to the region of the highest field strength. The value of $\chi$ is positive and independent of temperature. Sometimes paramagnetic substances follow the Curie law,

$$\chi = C/T \quad (6.9)$$

where ‘C’ is Curie constant.

Very few systems obey Curie law accurately. Often it is possible to describe the behavior of magnetic susceptibility as a function of temperature over a wide range by means of modification of Curie law called Curie Weiss law.

$$\chi = \frac{C}{T + \theta} \quad (6.10)$$

where ‘$\theta$’ is the deviation from Curie Weiss law.
Magnetic properties of crystal are frequently discussed in terms of the quantity called the magnetic moment $\mu_{\text{eff}}$ rather than susceptibility. The magnetic moment is related to the susceptibility

$$\mu_{\text{eff}} = 2.83 \chi_M \cdot T \quad (6.11)$$

where $\chi_M' = (\chi_M + \text{diamagnetic correction})$

(iv) **Ferromagnetism and antiferromagnetism**

In the most paramagnetic samples the magnetic properties originate entirely from the individual magnetic centers. Such samples where there is no secondary magnetic interaction between the neighboring paramagnetic centers are called magnetically dilute. Such interaction in a magnetically concentrated system may either lead to (a) decrease or (b) increase in magnetic moment. In case (a) the sample is called antiferromagnetic and in case of (b) the sample is said to be as ferromagnetic.

(iv) **Super Paramagnetism**

When ferromagnetic and antiferromagnetic materials are heated above critical temperature ($T_c$ and $T_N$) they change over to paramagnetic behavior. In contrast, super paramagnetic systems when cooled below a critical temperature will experience a very slow relaxation time. Super paramagnetism is observed in very small particles of transition metals and their compounds particularly their oxides. It can be used to characterize fine dispersions of metals, alloys and their oxides and has several applications $^{[33]}$.

(v) **The Techniques**

The techniques namely, the Gouy method, the Faraday method, NMR method, Magnetic anisotropy and Null deflection method for crystals are known to study the magnetic moments. Out of these techniques Gouy method, Faraday method and NMR method are widely used for determining the magnetic susceptibility of coordination compounds. The Gouy methods are the simplest of all. The Gouy method $^{[34]}$ used for determining magnetic susceptibility, consists essentially of suspending a cylindrical sample of a
Chapter 6 Electrical and magnetic study of crystal

substance in a non homogeneous magnetic field with the lower end in the region of maximum field and the upper end in a region of effectively zero field and measurement of the force exerted on the sample is made by the conventional weighing technique.

Magnetic susceptibility measurements in the present study were made at room temperature (30°C) using Satorius Semi micro Gouy balance.

The sample was weighed in presence and in absence of applied magnetic field (4 and 6 amperes) and from the difference in weights observed; the magnetic moment (µ_{eff}) of the sample was easily calculated. The gram susceptibility (χ_g) was calculated using the equation

\[ \chi \times 10^{-6} = \frac{\alpha + \beta \cdot dw}{W} \]  \hspace{1cm} (6.12)

Where, \( \alpha \) = correction due to displaced air
\[ \alpha = 0.029 \times 10^{-6} \text{ c.g.s. units } \chi \text{ volume of air} \]
\[ \beta = \text{Gouy tube constant} \]
\[ dw = \Delta W - \delta \]  \hspace{1cm} (6.13)

Here \( \Delta W \) is apparent change in weight (in mg) of the Gouy tube containing \( w \) gms of the sample after application of field, while \( \delta \) is deflection observed in weight of the tube after application of the field. The molar susceptibility \( \chi_M \) is obtained by multiplying the gram susceptibility \( \chi_g \) by the molecular weight of crystal. Pascal’s constants were used to apply diamagnetic corrections to obtain corrected molar susceptibility, \( \chi_M' \). The effective magnetic moment was then calculated using the following expression

\[ \mu_{eff} = 2.93 \left( \chi_M' \times T \right)^{1/2} \]  \hspace{1cm} (6.14)

where, ‘T’ is the temperature in Calvin.

Measurements of magnetic susceptibility have been of great value in determining bond types and structures of crystals\(^{[35,36]}\). The various types of bonding possible in a given crystal may often be distinguished on the basis of
the number of unpaired electrons present with each type. If experiment establishes the magnetic susceptibility and thus the number of unpaired electrons, questions may frequently be settled concerning orbital hybridization, degree of covalent character and probable structure. Theories of bonding, orbital and structure in coordination chemistry have not been thoroughly evolved, but magnetic data constitute a powerful tool for the improvement of current ideas.
6.3 EXPERIMENTAL

To measure electrical conductivity of all crystal a crystal were combined and form a tabulate of 6 mm diameter. Tabulate form of crystal was prepared at S. K. Patel college of Pharmaceutical Education and Research, Ganpat University, Kherva, Gujarat. A rotary Tablet machine was used to prepare tabulate of crystals.

![Rotary Tablate Machine](image)

**Figure 6.3 - Rotary Tablate Machine**

Specification:
- **Type:** Minipress – MT – 11
- **Pressure:** Hydrostatic
- **Company Made:** Karnavati Engineering Pvt. Ltd., Mehsana
- **Minimum Quantity:** 100 mg.
- **Maximum Quantity:** 1000 mg.
- **Used Tool:** B-Tolling (6 mm Diameter)
An electrical conductivity of all crystals was measured at Department of Chemistry, S. P. University, V. V. Nagar, Gujarat. High resistance electrometer was used to measure electrical conductivity shown in figure – 6.3. The temperature was varied for measurement of conductivity of all crystals.

Figure 6.4 - High Resistance Electrometer

Model Make: Keithley, Germany
Mode: Dynamic
6.4 RESULT AND DISCUSSION

An electrical conductivity of all crystal was measure at different temperature. A uniform thin layer of silver paste was applied on both the sides of the pallet of crystals, providing electrical contacts. Average diameter and thickness of each pallet were measured and found 6 mm. The pallet was firmly pressed between two circular metal disks functioning as electrodes. The other ends of electrodes were passed through the pallet holder for connections. The entire assembly was placed in a furnace. It was heated at a 1°C / min. Examination of result presented in Table – 2 reveals that the electrical conductivity of all crystals from \(10^{-5}\) to \(10^{-6}\) \(\Omega^{-1}\) cm\(^{-1}\) at 25°C. Thus the conductivity of all crystal increases with increases with temperature, slowly initially and very rapidly after some point between 400°K to 500°K depending upon the nature of material used to prepare crystal. The plots of electrical conductivity versus \(1/T\) shown in figure 6.5 to figure 6.7. For all the samples are found to be near about linear in the higher temperature range, the temperature at which this occur designated as the break temperature. It is worth noting that the electrical conductivity of crystals is highly dependent on the nature of material structure, the nature of metal and the size and shape of the ligand associate with crystal. In the present cases there would be linear structure of the crystal because the crystal formed through metal and schiffbase. However the results of our electrical conductivity measurements of all of the crystals reveal that they can be ranked as semiconducting materials with high resistance.

In the present study, the magnetic moment values have been carried out at room temperature for all crystals. The magnetic measurements data of the crystal are presented in Table - 4.5. In the present study, crystals of Ni(II), Fe(III) and Cu(II) are found to be paramagnetic in their character from the values of magnetic moments. Also these values of magnetic moments give
indication of the octahedral geometry for Fe(III), crystal and tetrahedral geometry for Cu(II) and Ni(II) crystals.

Table 6.1 - Electrical Conductivity of Crystals at Temperature

<table>
<thead>
<tr>
<th>1/T (°K)^{-1}</th>
<th>Electrical conductivity (mho per cm) of crystals (at temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Cu·L₂]·2H₂O·Cl₂</td>
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<tr>
<td>3.24</td>
<td>1.31x10^{-5}</td>
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<tr>
<td>3.09</td>
<td>1.32x10^{-5}</td>
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<tr>
<td>2.19</td>
<td>1.30x10^{-5}</td>
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<td>2.36</td>
<td>1.64x10^{-5}</td>
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Figure 6.5 - Electrical conductivity curve of \([\text{Cu}\cdot\text{L}_2] \cdot 2\text{H}_2\text{O} \cdot \text{Cl}_2\) crystal
Figure 6.6 - Electrical conductivity curve of [Fe\(\cdot\)L\(_2\cdot\)2H\(_2\)O] \cdot \text{Cl}_3 \text{ crystal}
Figure 6.7 - Electrical conductivity curve of [Ni·L$_2$]·4H$_2$O Cl$_2$ crystal
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