INTRODUCTION

I. INTRODUCTION

I. 1. Semiconductivity and Semiconductors :

(i) General :

The electrical conductivity (σ) is defined as the rate with which the charge is transported across a unit cross-sectional area per unit electric field applied. The conductivities of different types of materials are given in the "conductivity spectrum" (fig.1).

The term " Semiconductor " implies a defination namely, that it is a material having electrical conductivity intermediate between that of metals and insulators. At room temperature, the conductivities characteristic of metals are of the order of 10^{4} to 10^{6} ohm^{-1} cm^{-1}, whereas those of insulators range from 10^{-22} to 10^{-10} ohm^{-1} cm^{-1}. The semiconductors generally have conductivities from about 10^{-9} to 10^{3} ohm^{-1} cm^{-1}.

(ii) Conductivity equation :

The conductitity is proportional to q the amount of charge per c.c. and mμ the velocity of charge transport across a unit cross-sectional area per unit applied electric field.

Hence,

$$\sigma = q \times m\mu .... \qquad (1)$$

Since $q = n \times Z \times e$

where n is the density of charge carriers and Ze is the net charge carried by each carrier,

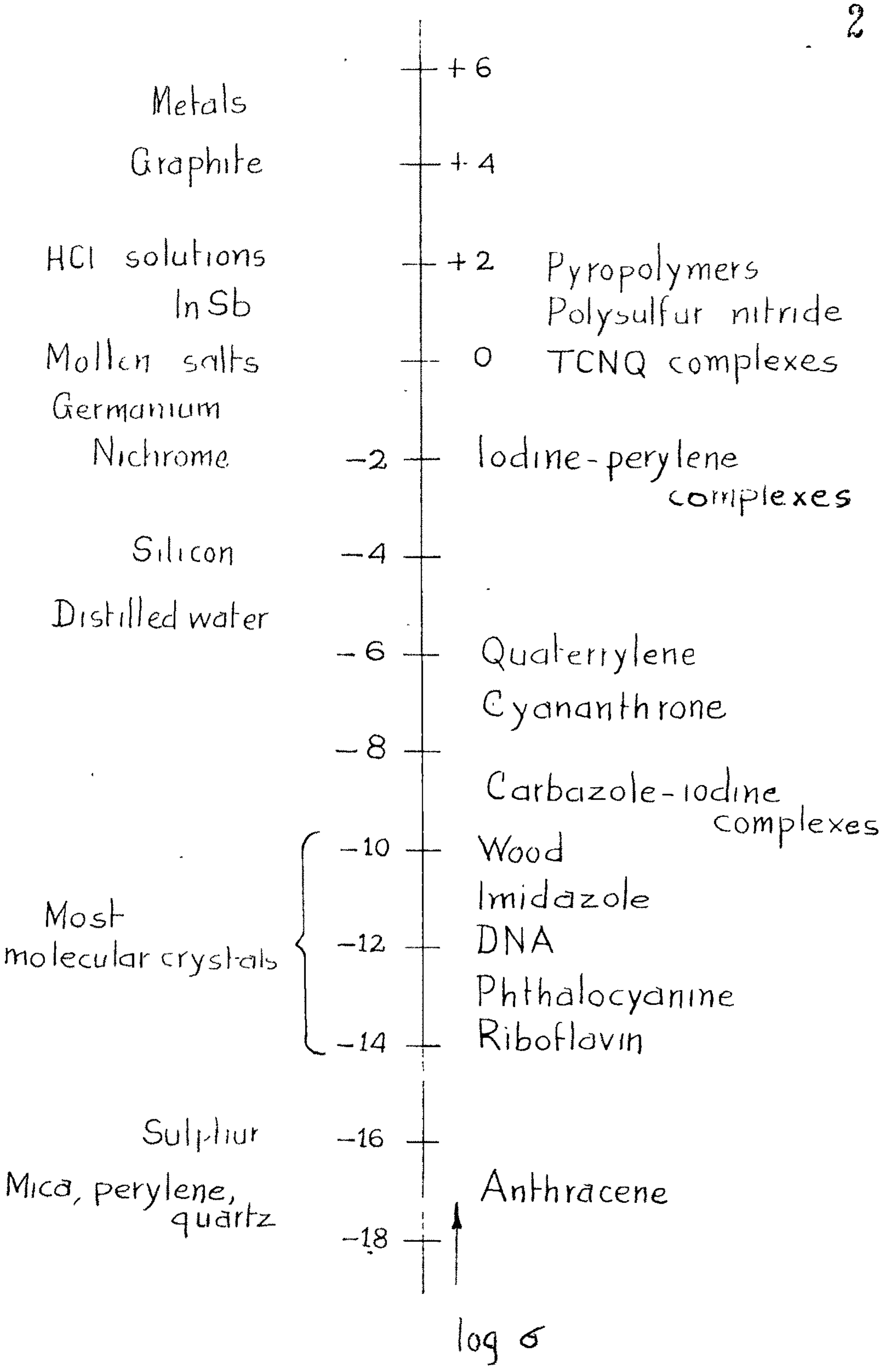

FIG. 1: CONDUCTIVITY SPECTRUM

$$\sigma = n \times Z \times e \times m\mu \; .... \qquad (2)$$

In general, more than one species of carriers (both positively and negatively charged carriers) may be present. Assuming that there is only a negligible interaction between the different carrier species, so that each moves as if others were absent, we can write the total net conductivity of the medium as

$$\sigma = \sum (n_i \times Z_i \times e \times m\mu_i) ..... \qquad (3)$$

where the summation is extended over all species of the carriers.

This equation applies well to most of the systems.

Because the mobility $m\mu$ may be different for different spatial directions in an anisotropic medium, the conductivity may also be anisotropic.

(iii) Electrons and Holes :

The charge carriers may be charged atoms (i.e. positive or negative ions), electrons or regions of space from which negative charges have been removed, the latter being termed as (positive) holes. The hole moves in the electric field like a positive charge. If the conductivity is predominantly due to ions, we call it ionic conductivity. On the other hand, electronic conductivity will be largely due to electrons and / or holes.
Electron is free if there exist energy levels available to it, into which it may go and can abstract energy from the applied electric field. The current carriers are those

electrons and holes which are free and the conductivity is determined by concentration of free carriers, their charge and their mobility.

(iv) Energy bands :

The quantitative features of semiconduction have been explained in terms of " energy bands ", which constitute the allowed electronic energy levels in crystalline solids and which relate to the interatomic binding.

Free atom approach :

If we bring two hydrogen atoms (H_A and H_B) close together so that their wave functions ψA and ψB overlap, it is found that combination of the two wave functions describe two new electronic wave functions for the pair of atoms as represented in fig.2.

The separation of the two levels increases as the spacing between the two atoms decreases. Figure 3 represents electronic energy levels when two hydrogen atoms (H_A and H_B) are allowed to approach close proximity, to form hydrogen molecule. If a group of six atoms, all in a row, is treated in the same way, we would find the same splitting of levels. Figure 4 shows energy levels corresponding to six 1 S states. Corresponding energy levels for 2 S states are also shown.

With an assembly of N-atoms, the same behaviour is observed. The spacing of the electronic energy levels within a group becomes small for large N, but the gap between the groups of levels is preserved. The closely

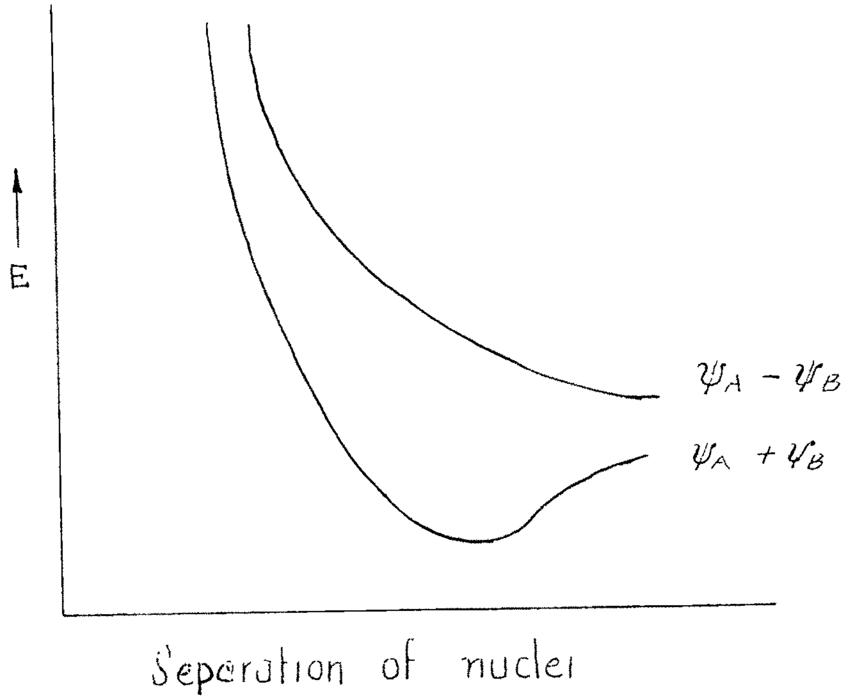

FIG. 2: E vs SEPARATION OF TWO NUCLEI

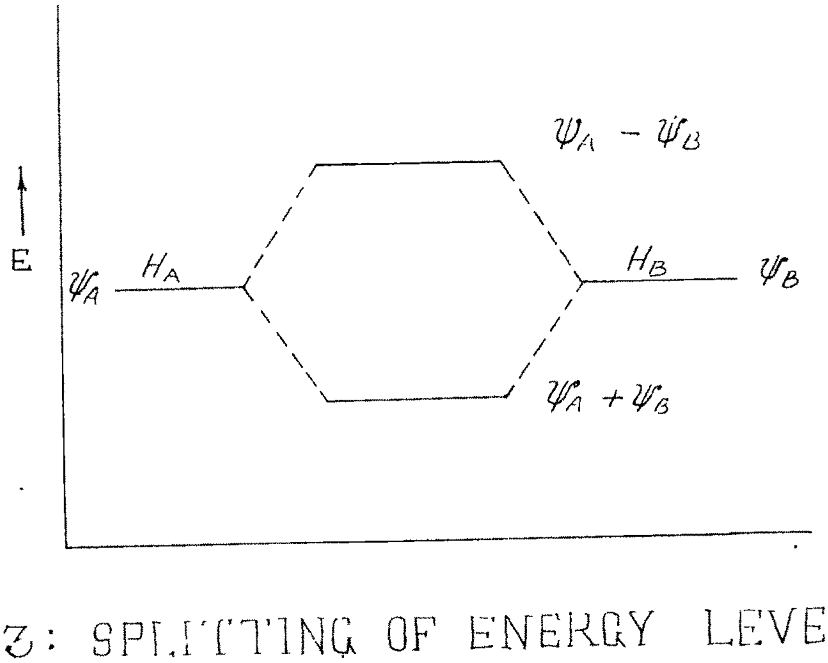

FIG 3: SPLITTING OF ENERGY LEVELS OF TWO HYDROGEN ATOMS APPROACHING CLOSE PROXIMITY

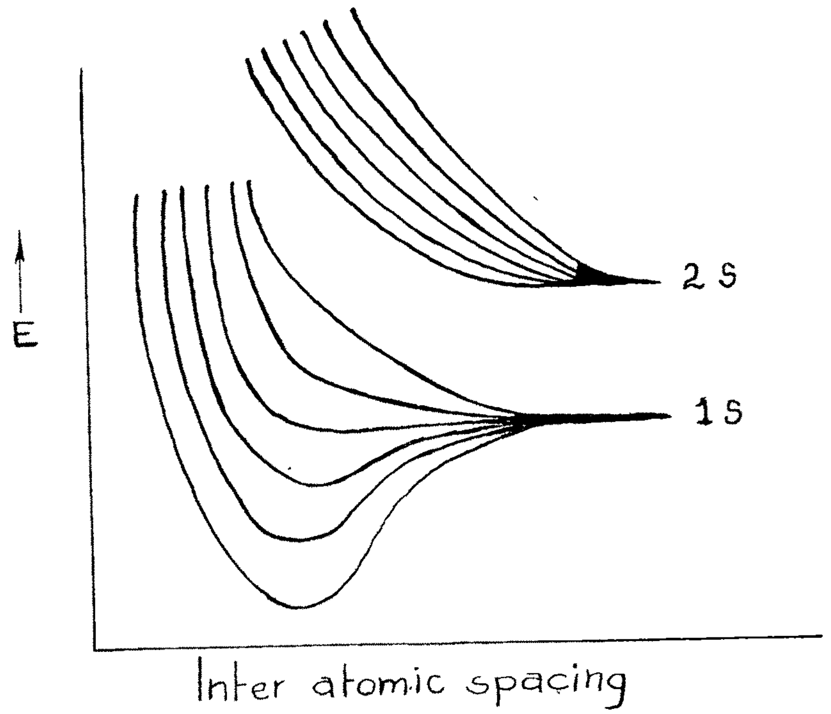

FIG. 4: ENERGY LEVELS CORRESPONDING TO 1S AND 2S STATES FOR SIX ATOMS IN A ROW.

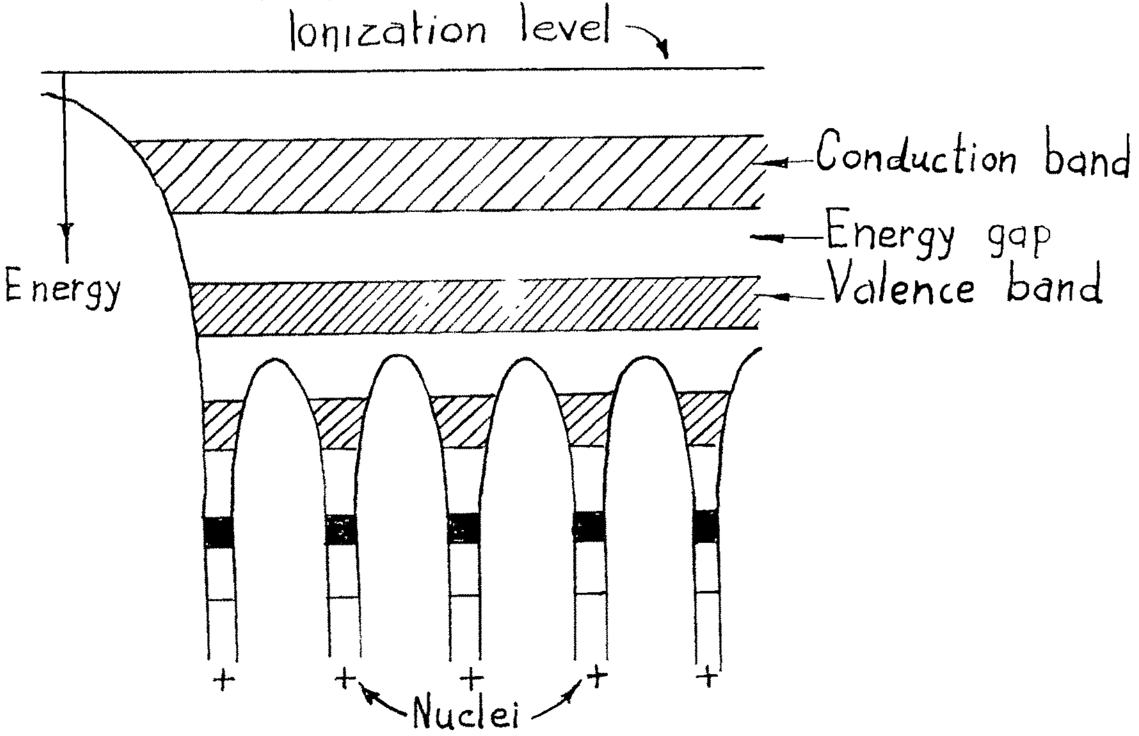

FIG. 5: ENERGY BAND IN A SOLID.

spaced energy levels form an " energy band " with " energy gap " or " forbidden gap " between the bands.

In the solid state, a large number of atoms exist in close proximity to each other. Hence, various allowed electronic energy levels form allowed energy bands. The valence levels produce a valence band and the allowed higher energy levels (excitation levels) produce a conduction band. These two energy bands are separated by an energy gap as shown in fig. 5.

We can now distinguish insulators, metals and semiconductors. In insulators, the valence band is full, the conduction band is empty and no free electrons are available to carry the current (fig.6). In a metallic conductor, the uppermost energy band containing electrons is only partially filled (fig.7) or a filled band overlaps an empty band (fig.8) and at least there is one valence electron per atom in these bands. These electrons are free to move in a field and since they are present in large numbers, they result in very high conductivities. A semiconductor stands between these two extremes. Electrical conductivity results from the (free)electrons and / or holes introduced into the solid by some means. The semiconductor differs from the insulator mainly in the reduced width of the energy gap (0.2 to 2.5 ev).

(v) Intrinsic Semiconductor :

A semiconductor may be either intrinsic or extrinsic. Any conductivity shown by the intrinsic semiconductor is due to electrons acquiring sufficient

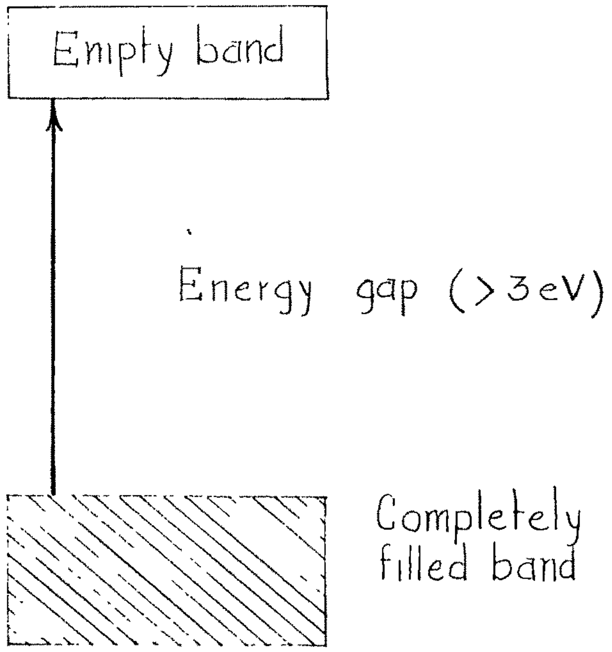

FIG. 6: INSULATOR

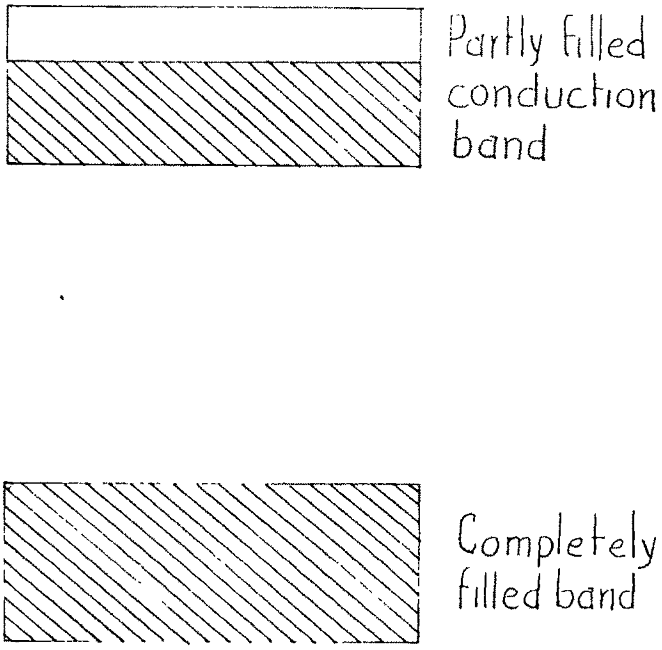

FIG. 7: MONOVALENT METAL

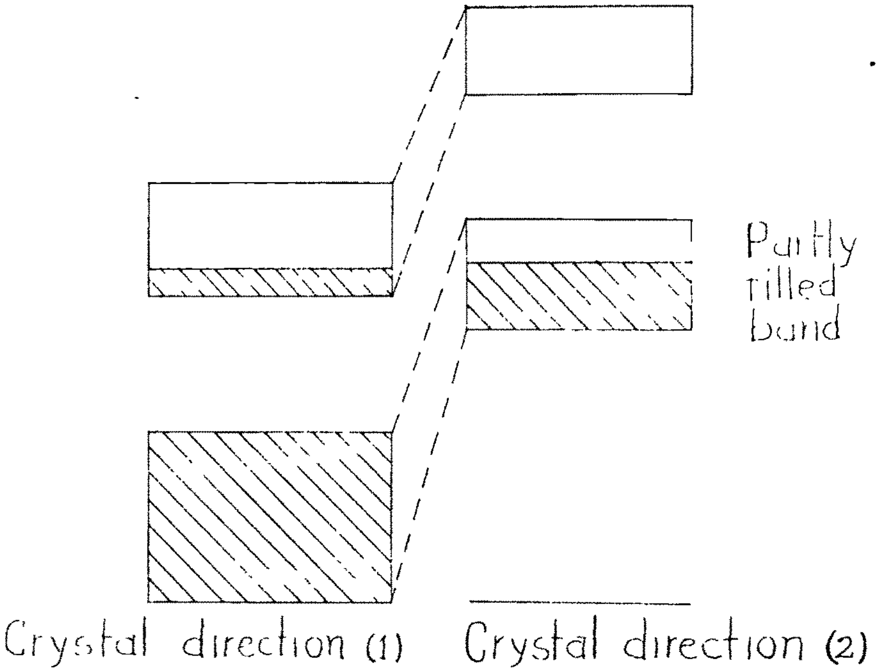

FIG. 8: BIVALENT METAL

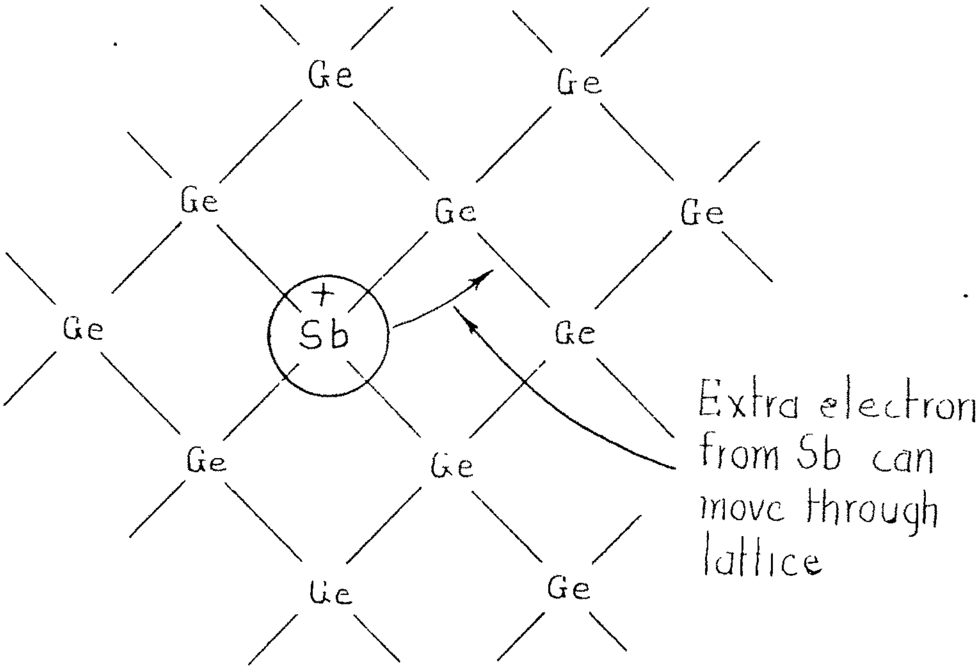

FIG. 9: IMPURITY SEMICONDUCTOR (n-type)

sufficient energy, in some way to cross the energy band. If the energy is supplied thermally, i.e. by some electrons interacting with the crystal lattice vibrations-the phonons so as to gain energy, we speak of thermal excitation ; if it is supplied by the absorption of a quantum of radiation, we speak of photon excitation ; and if it is supplied by an electric field, we call it field excitation. Excitation of an intrinsic semiconductor produces electron hole pair. The concentrations of both electrons and holes increase exponentially with temperature.

If n = no.of electrons / c.c., which will have energies equal to or greater than E_c

P = no.of holes / c.c., which will have energies equal to or greater than E_v

E_c = energy corresponding to the bottom of conduction band

E_v = energy corresponding to the top of valence band

E_f = energy corresponding to Fermi level

A, B, K = Constants,

$$n = AE^{1/2} K \exp\left[-(E_c - E_f)/kT\right]$$

and

$$P = BE^{1/2} K \exp\left[-(E_f - E_v)/kT\right]$$

For an intrinsic semiconductor

$$n = P = n_i \quad \text{and} \quad A \approx B$$

Therefore $E_c - E_f = E_f - E_v$

or $$E_f = \frac{E_c + E_v}{2}$$

(vi) Extrinsic Semiconductor :

Extrinsic semiconductivity is due to lattice imperfections or impurities. Frenkel defect and Schottky defect are the examples of lattice imperfections. They have profound influence on electrical properties of the crystal. In an impurity semiconductor, atoms are replaced by others of lower or higher valence. If the valence of the impurity atom is higher than that of the lattice atom (fig.9),one of the binding electrons of the impurity atoms will have no partner and thus will be weakly bonded to its atom. Little energy will be required to detach this excess electron, i.e. to ionize the impurity atom and give up the free electron to the conduction band (fig.10). Thus, introducing impurity atoms of higher valence creates free electrons having energies within the conduction band. It is equivalent to the introduction of an additional energy level within the energy gap,called donor level. The substance exhibits conductivity by virtue of free electrons and is called n-type (for negative sign of charge carriers).

Conversely, if the valence of the impurity is less than that of the parent lattice, a vacancy for electrons will be created which will be occupied by an

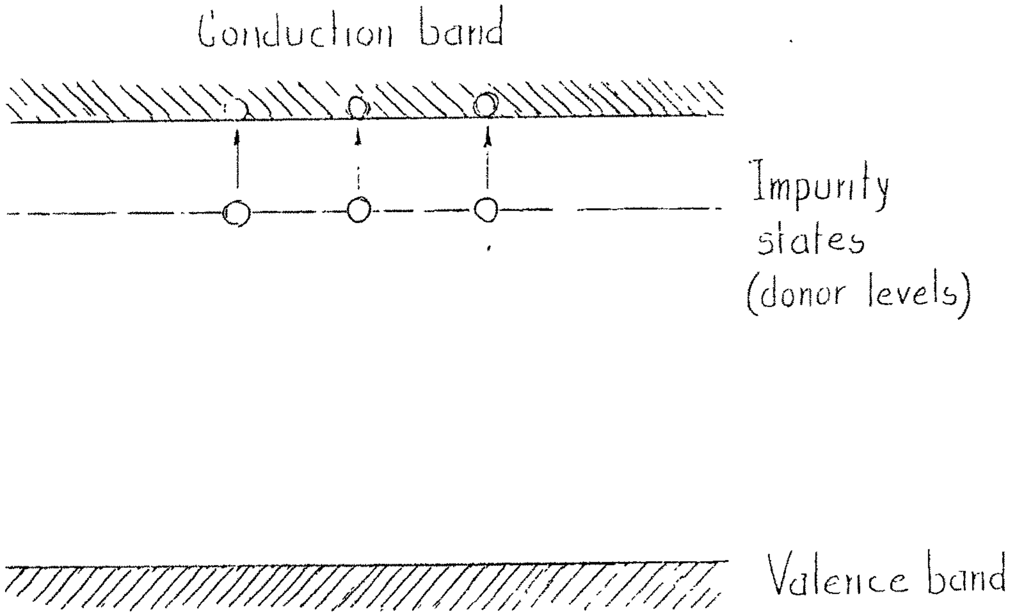

FIG 10: DONOR LEVELS IN n-type SEMICONDUCTOR

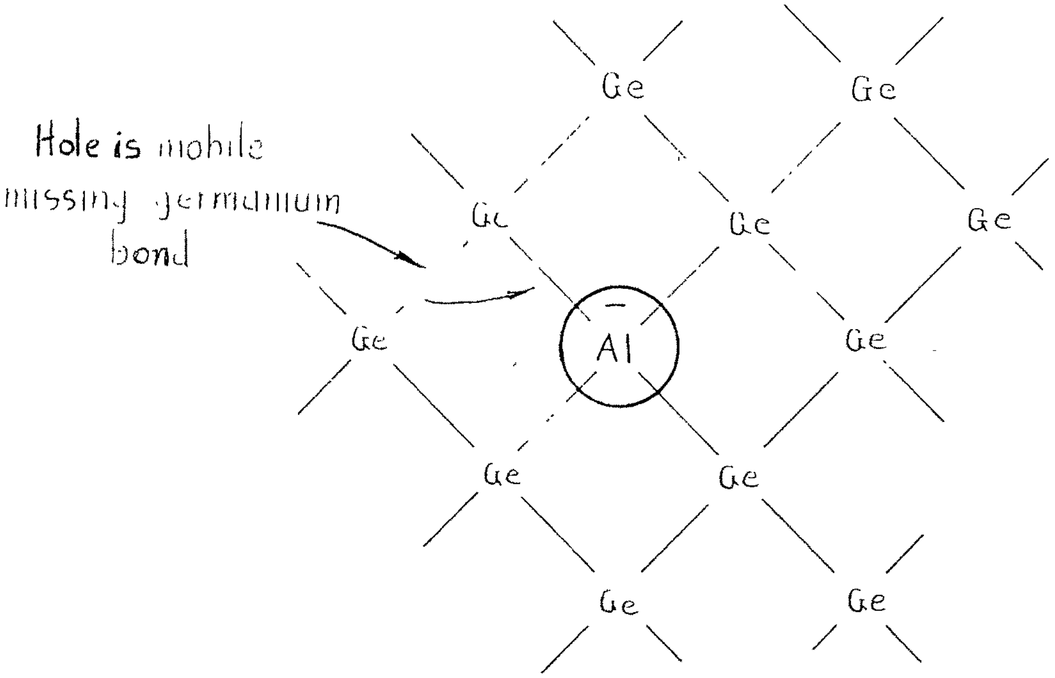

FIG 11: IMPURITY SEMICONDUCTOR (p-type)

electron. The vacancy is called a hole and may migrate through the crystal by diffusion and in fact behaves like a positively charged carrier (fig.11). An impurity having a valence lower than that of the parent lattice atom is called an acceptor impurity and it gives rise to energy level in the energy gap, called acceptor level(fig.12). The material is called p-type (for positive sign of charge carriers).

Let us consider an n-type semiconductor. At the absolute zero of temperature, all energy levels in valence band as well as those in donor band are occupied by electrons. The conduction band is empty and the crystal is an insulator. As the temperature is increased,electrons in donor levels gain sufficient energy from thermal excitation to jump into the conduction band and extrinsic conductivity is observed. As soon as the donor levels are completely emptied, the conductivity starts dropping as a result of phonon scattering, until the one set of intrinsic conduction, when it increases exponentially (with temperature). This behaviour is illustrated in fig.13.

I.2. Organic semiconductors :

(i) General :

Organic and organometallic compounds studied for their electrical conductivity and related properties in the last twenty years are tabulated with references as follows :

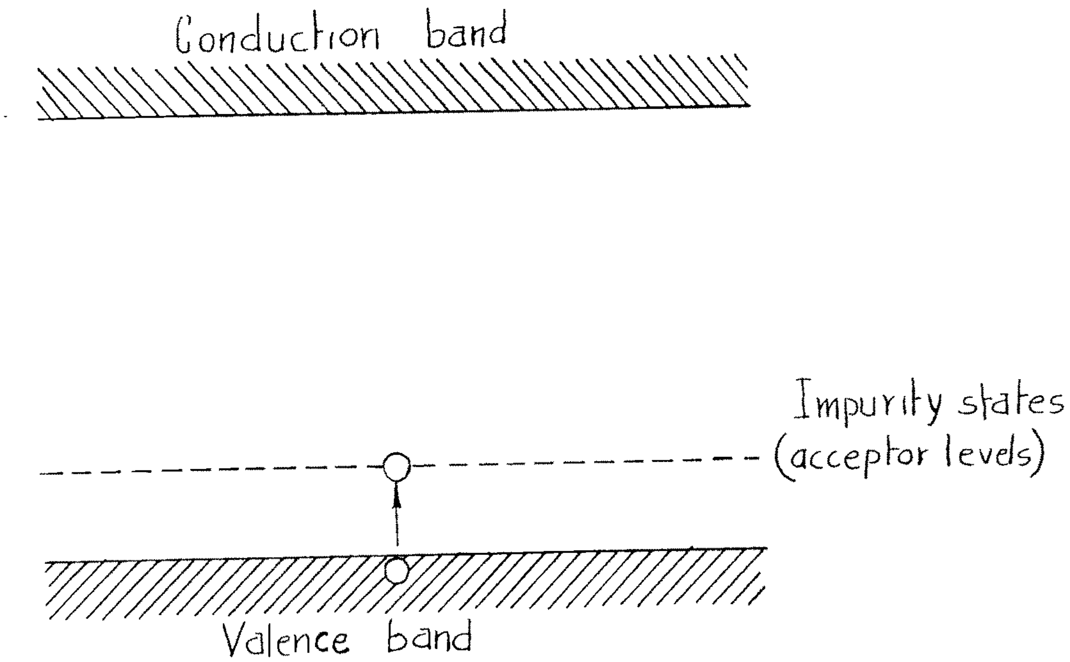

FIG 12: ACCEPTOR LEVELS IN p-type SEMICONDUCTOR

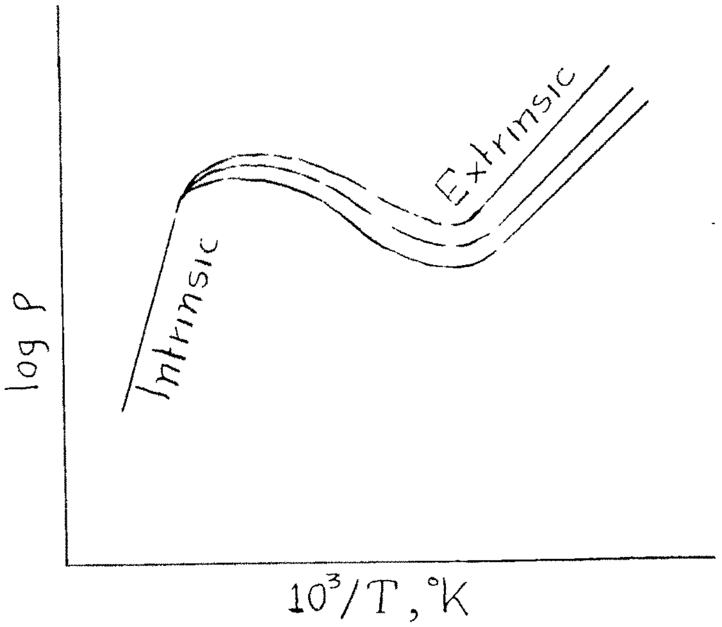

FIG.13: log ρ vs 1/T CURVES FOR A TYPICAL IMPURITY SEMICONDUCTOR

(a) Molecular crystals	... Table 1.
(b) Charge-transfer complexes ...	... Table 2.
(c) Coordination complexes ...	... Table 3.
(d) Polymeric substances including chelate polymers	... Table 4.
(e) Free radicals	... Table 5.
(f) Biological materials... ...	... Table 6.

(ii) <u>Brief survey</u> :

(a) <u>Molecular crystals</u> :

The resistivities of most of the molecular crystals are very high and there is a high degree of scatter in the values of E obtained by different investigators. The majority carriers in most cases are holes. Adsorbed and absorbed gases[229,230,231] exert a profound influence on the conductivity.

(b) <u>Charge transfer complexes</u> :

The charge transfer complexes generally have very low resistivities and very low energies of activation; however, their mobilities are comparable to those of molecular crystals. The majority carriers may be holes or electrons.

(c) <u>Coordination complexes</u> :

The activation energies of the metal complexes are similar to those of the metal free ligands. The resistivities of the complexes are, on the whole, lower by several orders of magnitude than those of the metal-free

Table 1

Molecular Crystals

Compound	Reference
Acridine	1
Anils	2
Anthracene	1,3,4,5 6,7,8,9, 10,11,12, 13,14,15
Anthranilic Acid	16
Benzanthrone	1,17
Benzene	18
Benzimidazole	19
Benzophenone	16
Benzoquinoline	1
Chloranil	20,21
Chlorpromazine	22,23,24
Chrysene	14
Coronene	15,25,26, 27
Cyananthrone	13
1,6-Diaminopyrene	28
Dibenzanthracene	29
Dibenzpentacene	30
Diphenylpentacene	
Dinaphthopyrene	15
Diphenyl	31
Flavanthrone	13
Fluoridine	32
Hexacene	15
Hydroviolanthrene	13
Imidazole	19
Indanthrazine	13
Indanthrone	
Iso-violanthrene	13,15,17 33,34,35 36
Iso-violanthrone	
Meso naphthodianthrene	37

Table 1 (Contd)

Compound	Reference
Naphthacene	15
Naphthalene	1,2,5,14, 38,39,40
Naphtho dianthrene Naphtho dianthrone	13
β-Naphthol	41
Ovalene	15,42
Pentacene	14,30,32
Perylene	14,27
Phenanthrene	1,43
1,10-Phenanthroline	1
Phenazine	1,19,29, 44
Phenothiazine	44
Phthalocyanine	7,20,45, 46,47,48, 49,50,51, 52,53,54
Pyranthrene	13,15
Pyrene	4,14,15
Resorcinol	55
Stilbene	12,56,57 58
Terphenyl	12,59
Tetracene	14
Tetra thiotetracene	60,61
Triphenodioxazine	32
Triphenyldiamine	56,58
Violanthrene	13,15,25 27
Violanthrone	13,34,35 46

Table 2

Charge-transfer Complexes

Electron acceptor	Electron donor	Reference
Benzoquinone	Benzidine,perylene,p-phenylene diamine,pyrene	62,63
Bromanil	p-Aminophenol,bromoaniline, pyrene,stilbene	64
	3,8-Diaminopyrene	65
	Dimethylaniline,tetramethyl p-phenylenediamine	35,66
	Tetrathiotetracene	60,67
Bromine	Aromatic hydrocarbons	68
	3,4-Benzoquinoline	69
	Brilliant green,crystal violet, malachite green	70
	Diaminopyrene	71
	Graphite	72,73
	Perylene,pyranthrene, violanthrene	35,74
	Pyrene	75
Chloranil	o-Aminophenol,p-bromoaniline, stilbene,[illegible]	76
	Carbazole	77
	Diaminodurene	78
	1,5-Diaminonaphthalene	78,79

Table 2 (Contd)

Electron acceptor	Electron donor	Reference
	Diaminopyrene	65,78, 79,80
	Dimethylaniline	35,66
	Diphenylamine	76,81,82
	Methylamine	83
	Oxinate.Pd(Cu)	84
	Perylene	79
	Phenothiazine	85
	Phenylenediamine	65,76,79, 86,87,88, 89
	Phthalocyanine	90
	Pyrene	64
	Tetramethyl benzidine	79
	Tetramethyl p-phenylenediamine	35,66
	Tetrathio tetracene	60,67
	Triethylamine	83
	Violanthrene	20
Chlorine	Aromatic hydrocarbons	68
	Brilliant-green,crystal-violet,malachite green	70
Dibromo-di-cyano-p-benzoquinone or	Dibenzo (c,d) phenothiazine	60,79,80

Table 2 (Contd)

Electron acceptor	Electron donor	Reference
Dichloro-di-cyano-p-benzoquinone		
Dichloro-di-cyano-quinone	Ferrocene	91
Dinitro-durene	p-Phenylenediamine	92
Fluoranil	Perylene	79,93
	Tetramethyl benzidine	79
Fluorine	Carbon	72
Hydroquinone	Phenazine	94
Iodanil	3,8-Diaminopyrene	65
	Dimethylaniline, tetramethyl-phenylenediamine	35,66
Iodine	Aromatic hydrocarbons	68
	Anthracene	95
	Benzidine	86,96,97
	Benzophenothiazine, N-methyl-phenothiazine, phenothiazine	60
	Cobaltocene	92
	Coronene	65
	Crystalviolet, malachite green	70
	Diphenylamine	81
	Iso-violanthrene	33

Table 2 (Contd)

Electron acceptor	Electron donor	Reference
	1,5-Naphthalenediamine, o-toluidine	96,97
	Perylene	35,79,98
	p-Phenylenediamine	48,99
	Cu-phthalocyanine	100
	Pyranthrene	35
	Pyrene	98
	Violanthrene	20,35,101
Iodine-monochloride	Iso-violanthrene	33
Maleic anhydride	Diphenylamine	81
Metal halide	Iso-violanthrone	33
Oxygen	Mesonaphthodianthrene	37
Quinone	Aromatic hydrocarbons	68
Tetrachloro-p-dipheno-quinone	Ferrocene	80
Tetracyano-ethylene	Acenaphthene, anthracene, azulene, hexamethylbenzene, pentamethylbenzene	68,102
	Aromatics	68
	1,2(or 3,4)benzpyrene	103

Table 2 (Contd)

Electron acceptor	Electron donor	Reference
	Cobaltocene, ferrocene	91
	Diphenylamine	81,82
	Naphthalene, perylene, phenanthrene, pyrene	102
	(Tetrahydro indenyl) iron	92
	Tetrathio tetracene	60
	Violanthrene	20,102
Tetracyanoquinodimethane	1,2 (or 3,4) benzpyrene	103
Tri-iodide	Carotene	105
Tri-nitro benzene	Aniline, anthracene, anthanthrene, p-chloroaniline, chrysene, dimethylaniline, p-phenylenediamine, pyrene, violanthrene	87
Tropylium bromide	Anthracene, hexamethyl benzene, naphthalene, perylene, phenanthrene	106

Table 3

Co-ordination Complexes

Metal	Ligand	Reference
Cu,Co,Zn	Dipyrro methene-1	104,107
Cu,Co,Ni	Dipyrro methene-2	104,107
Fe	Cyclopentadiene	56,58,108
Cu,Zn	Phthalimide	16
Cu	Phthalocyanine	26,39,46,47,49,52,54,100,109,110,111,112,113,114
Co,Fe,Mn,Ni	Phthalocyanine	49,52,115
Mg	Phthalocyanine	46,109
Pt	Phthalocyanine	111
Zn	Phthalocyanine	39,46,52,116
Nd	Phthalocyanine	117
Ni,Cu	Salen, Salphen	2
Ag	Azide	118
Cu	Tetra-2,3-pyridinoporphyrazine	110
Ni,Pd	Dioximes	119

Table 4

Polymers

Compound	Reference
Chelate Polymers	
-Bromanilic acid : Cu,Ni,Cd	120
-Chloranilic acid : Cu,Ni,Cd	
-1,5-Diacetyl-2,6-dihydroxy-naphthalene dioxime : Cu,Ni,Pd	121
-1,5-Diformyl-2,6-dihydroxy-naphthalene dioxime : Cu,Ni,Pd	
-2,4-Diacetyl resorcinol : Cu,Zn,Fe,Ni,Co,Cr,Pb,Sn	122
-2,4-Diacetyl resorcinol dioxime : Cu,Zn,Fe,Ni,Co,Cr,Pb,Sn	
-1,4-(or 1,5)Dihydroxy anthraquinone : Cu,Zn,Fe,Ni,Co,Cr,Pb,Sn	
-3,3'-Diacetyl-4,4'-dihydroxy-diphenyl dioxime : Cu	119
-2,5-Dihydroxy-p-benzoquinone : Cu,Ni,Cd	120,123
-1,5-Dihydroxy-phenazine : Cu,Ni,Cd	
-Dithiocarbamates : Cu,Co,Zn	124
-Dithiooxamide : Cu,Co,Ni	123,125,126,127
-Imidazole : Cu,Co,Zn	44
-Polythioamides : Cu,Ni,Co,Zn	128
-Quinoxalato phenazinium - Fe	129
-Thioamides : Cu,Co,Zn	124
-TCNE :Fe,Ag,Cu,Zn,Al,Hg,Ni,Ti,Co,Cd	130,131

Table 4 (Contd)

Compound	Reference
Polymeric Substances	
Bromo-dihydropolycyclopentadiene	132
Butadiene-styrene copolymer	133
Butadiene-acrylonitrile copolymer	
Cellulose, (pyrolyzed)	22
Diphenylamine polymers	134
Ferrocene-benzal copolymer	135
Ferrocene-polymers (polyketones)	
FeCl$_2$ polymer of chloranil : p-phenylene diamine	129
Graphite, pyrolytic	136
1-Methyl-2-picolinium polyiodide	71,23
1-Methyl-quinolinium polyiodide	
Nylon	137
Poly acenaphthalene : TCNE	103
Poly acenequinones	135,138
Poly acenequinone radical polymers	139,140
Poly acetylene	103,141,142,143
Poly acrylonitrile	144,145,146,147,148,149,150,151,152
Polyamide : TCNQ	153

Table 4 (Contd)

Compound	Reference
Poly amides	104,107,147, 154,155,156
Poly anilines	157
Poly anthracene	140
Poly azines	158
Poly azoaromatics	159
Poly azophenylenes	160,161
Poly benzenes	162
Poly benzimidazoles	142
Poly butadiene	133,163
Poly cyanamide ; Poly cyanic acid	164
Poly dehydrocondensation products of bis-acetylenes	165
Poly dibenzpyrene	140
Polyenes	166,167
Poly ethylene	168,169,170
Poly (azophenyl) ferrocene	171,172
Poly glycine	173
Poly imidazole (pyrolyzed)	174
Polymer dithiocarbamate (substituted)) Polymer thiocyanate (Cu,Co,Ni,Ag))	119,126,127
Polymer thiophene,(thioacetamide, pyrrole,pyrazole)	175
Polymeric condensation products of aromatic anhydride and hydroquinone	176

Table 4 (Contd.)

Compound	Reference
Polymer from TCNE with metals or metal compounds	177
Poly naphthalene	30
Poly phenanthrene	140
Poly phenyl	135
Poly phenylene	178,179
Poly phenylene : TCNQ	180
Poly phthalocyanine : (Cu,Sc,Zr,Co,Fe, Zn)	130,181, 182,183
Poly propylene	170
Poly propyne	142
Poly pyrene	140
Poly pyridines, (substituted)	174
Poly schiff bases	184,185, 186,187
Poly schiff bases, Cu and Ni	2
Poly styrene	5,133
Poly styrene. $AgClO_4$ atactic	104
Poly sulfer anthracene	162
Poly sulfer nitride	188
Poly phenylthioether (substituted)	135
Poly (vinylacetate)	169,189,190
Poly vinylacetylene	179
Poly vinylalcohol	191
Poly vinylalcohol,metal chelates	192

Table 4 (Contd)

Compound	Reference
Poly vinylanthracenes	193
Poly vinylcarbazole	194
Poly vinylcarbazole : TCNQ	180,194
Poly vinylchloride	170,195,196
Poly vinylene, poly (vinylpyridine)I_2	178
Poly vinylidene chloride	170
Poly vinylmesitylene	103
Poly vinylnaphthalene, poly vinylnaphthalene (substituted)p-benzoquinone, poly vinylnaphthalene : TCNE	103
Poly vinylpyridine : TCNQ	153,180,197,198,199
Reaction product-pyromellitonitrile and methanol or hydrogen sulfide	182,200
Reaction product- trinitrobenzene and iodine	193
TCNE polymer	201,202
TCNQ : polyaromatics	180
Tetramethyl ammonium-polyiodide Triphenyl ammonium polyiodide	23,71
Xanthene polymer	203

Table 5

Free Radicals

Free Radical	Reference
Banfield and Kenyon's radical	204
α,γ-bis diphenylene-β-R-phenyl allyl radical	205
Coppinger's radical, Galvinoxyl	204,205,206
4-Cyano-N-methyl-quinolinium $(TCNQ)_2$	207
Diamino durene $(TCNQ)_2$	
Diamino pyrene (TCNQ)	208
Dihydroxyquinolinium (TCNQ)	207
Diphenyl picryl hydrazide	36,205,209,210, 211,212,213,214
Metal:$(TCNQ)_2$: Ba,Mn,Fe	207
Metal:(TCNQ) :Cs,Cu,Li,Ag,Na	
N-Methyl-2,3-(or 3,4 or 7,8) benzo-quinolinium $(TCNQ)_2$	103
N-Methyl quinolinium : $(TCNQ)_x$ (x =1 or 2)	207
Morpholinium (TCNQ)	
Quinolinium $(TCNQ)_2$	
Triethyl ammonium (TCNQ)	
Trialkyl ammonium $(TCNQ)_2$ (methyl, ethyl)	
Triphenyl methyl arsonium $(TCNQ)_2$	
Triphenyl methyl phosphonium $(TCNQ)_x$ (x = 1 or 2)	
2,4,6-Triphenyl perylium $(TCNQ)_2$	
Violanthrone - B	35

Table 6

Biological Materials

Compound	Reference	Compound	Reference
Adenine	215	Collagen	39,104
Adenine phosphate,	216		107,224
Adenosine,		Chloro-	104,
Adenosine tri-		porphyrin-III	107
phosphate		Cytidilic acid	216
Adenylic acid,		Cytidine	
yeast		Cytochrome-C	104,107
Adenylic acid,			225
muscle		Cytosine	215
Aetio porphyrine-	104,	DNA	104,107
1,Cu,Co,Mg,Ni	107	DNA hearing	224
Alanine	217	sperm	
Albumen,Serum	39,218	DNA-Na salt	215,226,
Bovin plasma	104,		227
albumen	107	Diketo -	217
Calf thymus	219	piperazine	
Carotene	220	Edestin	39
Carotene,O_2	220	Elastin	104,107
complex		Fibrinogen	39,104,
Chlorophyll	221,222		107
Chlorophyll-	220	Gelatin	5,104,
protein complex			107,220
Chloroplasts	223	Globin	217

Table 6 (Contd)

Compound	Reference	Compound	Reference
Glycine free and Cu chelate	217	Poly-L-tyrosine, helical and random coil	104, 107
Guanine	215	Protein dry	137
Guanylic acid, Guanosine	214	RNA-yeast	104, 107
Hematin	217	Rhodopsin	220
Hemoglobin	104,107, 217	Riboflavin	216
Hemoglobin, dry bovine	220	Thrombin	104, 107
Hemoglobin,ferro	217	Thymidine	216
Insulin,pig	104,107	Thymine	215
Keratin	137	Thymus nucleoprotin Tobacco mosaic virus	104, 107
Lysozyne	104,107	Tyrosine	217
Methemoglobin	217	Uracil	215
Myosin	224	Uridine, uridylic acid	216
Oxamide	217		
Plasma,bovine, chloranil complex	228		
Poly glycine	104,107, 217		

ligands ; and the mobility for the complexes, tends to be much higher than that for the metal-free ligands. In most cases the majority carriers are holes.

A considerable drop in resistivity as well as in activation energy is obtained upon changes in the peripheral part of the ligand ring systems[110].

(d) Polymers :

The polymers exhibit a wide range of resistivities, energies of activation, and mobilities. The values of resistivities and E are low for the pyro polymers ; and metal doping permits changes in the conduction properties of pyro polymers. Many coordination polymers owe their conductivity to a charge transfer interaction between the donor and acceptor atoms and their conductivity could be increased by using conjugated ligands.[120,121,122,123]

(e) Free radicals :

The free radicals usually have low resistivities and low mobilities. The majority carriers may be holes or electrons. It may be noted that the mere presence of one or more unpaired electrons does not suffice to ensure a high conductivity.

(f) Biological materials :

Biological materials usually have high values of resistivities and of the energies of activation. A difficulty in the evaluation of the experimental data on the biological materials is their very pronounced dependance on the presence of water.[217,220,232,233,234] Rosenberg,[220] for example, notes that the conductivity of crystalline hemoglobin increases from its dry conductivity by a factor of 10^{10} upon adsorption of 8 % by weight of water. The effect of drying a film of the sodium salt of deoxy ribonucleic acid[226] is illustrated in fig.(14). Both the resistivity and the energy of activation increase on drying.

I,3. Chelate polymers :

Dewar and Talati[121] studied the conductivity of polychelates of the dioxime of 1,5-diformyl(and 1,5-diacetyl) 2,6-dihydroxy naphthalene with Cu,Ni and Pd.

Kanda and Kawaguchi[123] investigated the electrical resistivity of the copper chelate polymers of rubeanic acid, 2,5-dihydroxy-p-benzoquinone and 1,5-dihydroxy phenazine.

Kanda[120] studied the electrical conductivity of the complexes of 1,5-dihydroxy phenazine, 2,5-dihydroxy-p-benzoquinone, chloranilic acid and bromanilic acid with Cu,Ni and Cd and observed low values of conductivity.

Terent'ev et al.[126] investigated the conductivity and activation energy for the chelate polymers prepared from tetrafunctional organic compounds and metal acetates. Copper polychelates showed the highest conductivity. Conductivity decreased and energy of activation increased in the order of cobalt,zinc and nickel.

Electrical conductivity of the chelate polymers prepared from 2,4-diacetyl resorcinol, 2,4-diacetyl resorcinol dioxime, 1,4 and 1,5-dihydroxy anthraquinone

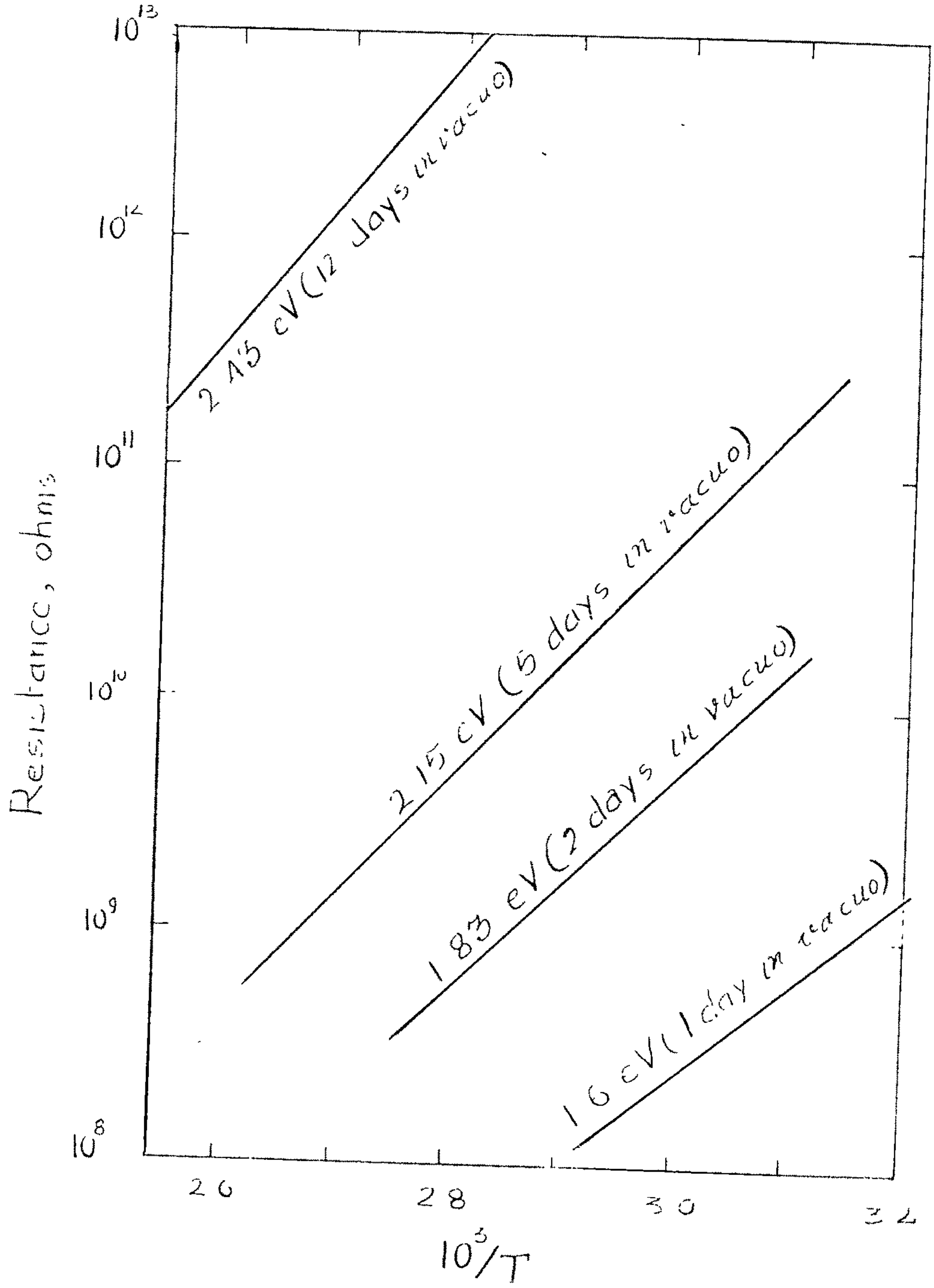

FIG. 14: RESISTANCE vs 1/T CURVES FOR Na-DNA PELLETS.

and 1,5-dihydroxy phenazine with Cu,Zn,Fe,Ni,Co,Cr,Pb and Sn have been studied by Inoue et al.[122] The resistivity was in the following order for each metal ion.

hydroxy ketone type < quinone type < phenazine type
The higher the ionization tendency of metal ion, the lower was the energy gap.

Chelate polymers of dithio carbamates and thioamides of pyridine derivatives with Cu,Co and Zn have been studied for electrical resistivity by Terent'ev et al.[124]

Brown and Aftergut[44] studied the polymeric copper,cobalt and zinc complexes of imidazole and suggested that an increase in the length of the conjugated system produced lower resistivities and energy gaps.

Bolto and Weiss[129] studied the electrical conductivity of Fe,Co,Ni,Cu,Zn,Cd,Mg,Ca,Ba,Ru,Os,Cr and Mn complexes of quinoxalophenazine. Fe as $FeCl_2$ gave the best conductor and also of the coordination polymers of transition metal ions with 4 ligands of the bis(8-hydroxy quinoline) type.

I.4. Aim and object of the present work :

Dewar and Talati[121] suggested that if a conjugated aromatic system is coupled with a suitable transition metal so that a polymeric chain is formed involving $d\pi$-$p\pi$ bonding, through-conjugation would result and such a system would possess interesting electrical properties. They showed that polymeric chelates formed by copper, nickel and palladium with bis-bidentate aromatic ligands such as the dioximes of 1,5-diacetyl -2,6-dihydroxy naphthalene possess semiconducting properties. They further suggested that if octahedral complexes are formed instead of square planar ones, the two trans positions should be blocked by ligands of some other type. We believed that these additional ligands will have an influence on (i) the orientation of molecules (ii) inter molecular distance and (iii) the lateral binding of molecules. It will affect the semiconductivity of the chelate polymers.

As shown earlier only a few types of chelate polymers were investigated for their semiconductivity. Hence, it was considered interesting to prepare various chelate polymers possibly in octahedral state and to study their semiconductivity.

With a view to study these aspects, we planned,

(1) to prepare various bis-bidentate aromatic ligands,
(2) to prepare chelate polymers of these ligands with the transition metal ions,
(3) to prepare ammino derivatives of these chelate polymers,
(4) to prepare molecular complexes of halogens with complexes,
(5) to study the magnetic and spectral properties of the products and
(6) to study the electrical resistivity of the products over a range of temperatures.

Investigations carried out with the above points in view and the discussion of the results obtained are presented in the following pages.