

PHYSICS of SEMICONDUCTORS

A. F. IOFFE

*Member of the U.S.S.R. Academy of Sciences,
Director of the Institute of Semiconductors*



**INFOSEARCH LIMITED
LONDON**

Translated from Russian

A. F. IOFFE

"Fizika Poluprovodnikov", 491 pp., 1957.

Published by the Publishing House of the U.S.S.R.
Academy of Sciences, Moscow-Leningrad. Revised and
supplemented by Prof. A. F. Ioffe for the English edition.
Translation edited and indexed by H. J. Goldsmid.

© 1960 by Infosearch Ltd.

All Rights Reserved.

This book or any part thereof must not
be reproduced without the written per-
mission of the publishers.

Infosearch Ltd.
207 Brondesbury Park,
London, N.W.2.

Distributed outside the U.S.A. by

Cleaver Hume Press Ltd.
31 Wrights Lane, London, W.8.

PHYSICS OF SEMICONDUCTORS

List of Symbols

IN the following list the various symbols are defined as they are most commonly employed in the book. However, in some cases it will be found that a symbol may have a meaning differing from that given below; in all such cases the interpretation of the symbol will be clear from the context.

A	constant in Hall formula,
C	constant in thermoelectric equation, constant of interaction,
D	diffusion coefficient,
D_e	diffusion coefficient of current carriers,
E	energy,
\mathcal{E}	electric field,
ΔE_0	energy gap,
ΔE	impurity activation energy,
$\Delta E'$	distance of Fermi level from band edge,
E_1	energy at top of valence band,
E_2	energy at bottom of conduction band,
E_ϕ	energy at Fermi level,
F	free energy, force,
H	magnetic field,
H_c	coercive force,
I	angular momentum,
J	electric current,
K	thermal diffusivity,
L	length, diffusion length, barrier layer thickness, light intensity,
M	ionic or atomic mass, magnetic moment,
N	excess impurity concentration, density of ions, Nernst coefficient,
N_0	number of atoms per cm ³ ,
N_1	donor concentration,
N_2	acceptor concentration,
N_{eff}	effective density of states,
P	momentum,

Q	quantity of electrons, quantity of heat,
R	Hall coefficient, resistance,
S	cross-section area, entropy, Righi-Leduc coefficient,
T	absolute temperature,
T_k	Fermi temperature,
T_K	Curie temperature,
T_1	hot junction temperature,
T_2	cold junction temperature,
U	energy, ionization energy,
V	volume, voltage or potential difference,
V_c	contact potential difference,
V_n	polarization voltage,
a	lattice constant,
c	specific heat, velocity of light,
c'	thermal capacity per unit volume,
e	electronic charge,
f	perturbed Fermi function,
f_0	equilibrium Fermi function,
g	spectroscopic splitting factor,
h	Planck's constant,
j	current density,
k	optical absorption coefficient, Boltzmann's constant, wave number,
l	free path length,
m	mass of carrier,
m_0	free electron mass,
m_-^*	effective mass of electrons,
m_+^*	effective mass of holes,
n	refractive index, carrier density,
n_0	intrinsic electron concentration,
n_-	electron concentration,
n_+	hole concentration,
p	proportion of filled states, pressure, exponent in temperature variation of mobility,
$p_{1,2,3}$	momentum coordinates,
q	rate of heating, charge,
$q_{1,2,3}$	space coordinates,
r	exponent of energy in expression for free path length,
t	time,
u	mobility,
v	electron velocity, velocity of sound,
x	absorption coefficient,
z	thermoelectric figure of merit,

α	thermoelectric power, temperature coefficient of energy gap,
γ	coefficient related to polarizability,
ϵ	dissociation energy of ion, dielectric constant, kinetic energy of electron,
ζ	coefficient of performance,
η	efficiency,
θ	Debye temperature,
κ	thermal conductivity,
κ_1	lattice component of thermal conductivity,
κ_2	electronic component of thermal conductivity,
λ	wavelength, $-\mu/kT$,
$\bar{\lambda}$	mean free path of phonons,
μ	chemical or Fermi potential, Bohr magneton, permeability,
ν	frequency of vibration,
Π	Peltier coefficient,
ρ	electrical resistivity, space charge density, density,
σ	electrical conductivity, secondary emission coefficient,
σ_p	photoconductivity,
τ	relaxation time, Thomson coefficient,
$\bar{\tau}$	electron or hole relaxation time,
τ_0	lifetime,
ϕ	work function,
χ	magnetic susceptibility,
ψ	wave function,
ω	barrier energy.

Contents

LIST OF SYMBOLS	ix
CHAPTER 1. SOLID ELECTROLYTES	1
Movement of charge in electrolytes	1
The nature of the current carriers	2
The current mechanism in solid electrolytes	5
Concentration of charge carriers	9
Temperature dependence of the conductivity	11
Ion mobility	13
Crystal lattice defects	15
Impurities	16
Chemical nature of the current carriers in ionic crystals	17
Mixed ionic and electronic currents	19
High-voltage polarization	20
The effect of ionic currents in electronic conductors	22
CHAPTER 2. METALS	24
The motion of electrons	24
Electron mobility	25
The effect of temperature on electron mobility	26
Thermal conductivity	27
Temperature dependence of the conductivity	30
Electron theory of metals	32
Quantum statistics of electrons in metals	34
Velocity distribution of electrons	35
The effect of temperature	37
Energy distribution of electrons	38
Degeneracy of the electron gas	41
Heat capacity of electrons	42
Quantum states of the electrons in an atom	43

Quantum states of electrons in a metal	44
X-ray spectra of metals	45
Distribution of electron velocities in an electrical field	49
Thermionic emission	51
Magnetic properties of electrons	55
Thermoelectric phenomena	56
 CHAPTER 3. ELECTRONIC SEMICONDUCTORS—A GENERAL SURVEY	 59
Types of semiconductor	59
Comparison with electrolytes	60
Comparison with metals	61
Sign of the current carriers	63
Thermal equilibrium of the electrons in a semiconductor	66
Temperature-dependence of the electron concentration and electrical conductivity	68
The effects of impurities on the conduction mechanism and electrical conductivity	69
Photoconduction	72
Volume photo-e.m.f.s.	79
Strong electric fields and breakdown	79
The barrier layer	82
The need for the quantum theory in studies on semiconductors	84
 CHAPTER 4. FUNDAMENTALS OF THE QUANTUM THEORY OF SEMICONDUCTORS	 87
The quantum states of electrons in a solid	87
Conduction electrons	91
The laws of motion for free electrons	96
The conditions of motion of an electron in a semiconductor	97
The laws of motion of electrons in a periodic field	99
The effective mass	100
The Brillouin zones	104
Holes and electrons	104
Carrier mobilities	109
Methods of measuring mobilities and effective masses	110
Additions to the electron theory of metals	111
The distribution of the electrons in a semiconductor among the quantum states	112
The free electron and hole concentrations	114

The chemical potential	116
The X-ray spectra of semiconductors	118
Semiconductors of low resistivity	119
Impurity levels	120
Surface states	125
Polarons	127
Excitons	128
The energy levels of semiconductors	129
The present state of semiconductor theory	132
 CHAPTER 5. PHYSICAL PHENOMENA IN SEMICONDUCTORS (PROPERTIES OF THE CRYSTAL LATTICE)	136
Short- and long-range order	136
Semiconductor crystal lattices	139
Imperfections in crystal lattices	148
Impurities	151
Thermal vibrations of the lattice	156
Scattering of electrons	167
Mean free path and mobility of electrons	173
The concentration of charge carriers	184
Properties of surface layers on semiconductors	188
Contact resistance	189
Solid rectifiers	196
Slow time-dependent phenomena in barrier layers	203
<i>p-n</i> junctions	205
Rectifiers and transistors	214
Transformation of light and nuclear radiation into electrical energy by means of <i>p-n</i> junctions	219
Emission of charge carriers from a semiconductor	221
The contact potential	228
External photo-effect	231
Thermionic emission	234
Secondary electron emission	237
Electron emission due to ions	240
Contact electrification	242
Semiconductors in electric and magnetic fields	243
Change of resistance in a magnetic field	249
Diamagnetism	257

Paramagnetism	258
Cyclotron or diamagnetic resonance	262
Ferromagnetism	266
Ferrites	270
Thermal conductivity of semiconductors	271
Thermoelectricity: discovery of thermoelectric phenomena	288
Calculation of the thermal e.m.f.	305
Thermoelectric generators	313
Thermoelectric cooling	318
Thermoelectric heating	321
CHAPTER 6. METHODS OF MEASURING THE BASIC PROPERTIES OF SEMI- CONDUCTORS	326
Electrical conductivity measurements	328
Mobility	331
Carrier concentration and effective mass	332
Forbidden band width and position of impurity levels	333
The lifetime and the diffusion length	335
The thermoelectric power	336
Thermal conductivity and heat capacity	337
The contact potential	342
Photoconductivity	344
The dielectric constant	346
CHAPTER 7. SEMICONDUCTING MATERIALS	349
The study of semiconducting materials	349
The classification of semiconductors	352
Atomic lattices with valence bonds	353
Molecular lattices	376
Sulphides, selenides and tellurides	381
Oxides	386
Ionic crystals	395
Alloys of metals	396
Liquid semiconductors	399
Organic materials	400
Semiconductor materials for thermoelements	401
CONCLUSIONS	423
SUBJECT INDEX	433

CHAPTER

1

Solid Electrolytes

Movement of charge in electrolytes

The mechanism of electrolytic conduction in aqueous solutions was thoroughly investigated and understood even in the 19th century. A similar mechanism was also established later for currents in many solid salts and their melts. It was found that currents in most glasses, in polymers and many insulating materials are also carried by ions.

Electric currents observed in such solids differ in many respects from currents passing through liquid solutions, despite the similarity of the charge carriers; in the solids the magnitude of the current for a constant potential difference usually decreases with time and often drops virtually to zero. When the source of the potential difference is removed, one observes appreciable reverse e.m.f.s, in closed circuits of many solid electrolytes, which attain values equal to the earlier applied potential difference; reverse currents appear even without the application of an external e.m.f. Sometimes these reverse currents transfer a quantity of electricity equal to that which has previously passed in the forward direction. Heat and light alter the electrical properties of such conductors, the changes sometimes being irreversible. These properties of dielectric crystals were discovered in the 19th century and studied in detail by Paul Curie.

As late as 1912 the foregoing phenomena were still regarded as abnormal manifestations of dielectric properties of insulators and not as a result of the movement of charges in the materials.

I have, however, succeeded in demonstrating that the process does not involve the dielectric displacement of charge within a molecule but the movement of charge across the bulk of the conductor, i.e. the flow of an electric current. The special features of the current in solid electrolytes are due to the accumulation of charges of one sign in the vicinity of the electrodes. The field set up by such a space charge is superimposed on the external field, thus leading to a change in the magnitude of the current.

When the space charge is duly taken into account the apparent anomalies disappear. The current obeys Ohm's law over a wide range

of potential differences, the current density being strictly proportional to the field strength. Solid electrolytes can therefore be described not only by their dielectric constant but also by a certain specific electrical conductivity which depends strongly on temperature and chemical composition, this dependence following certain definite laws.

My colleagues and I have succeeded in showing that the extensive scatter in the values of the electrical conductivity of individual specimens of ionic crystals may be attributed to different impurity contents. By repeated crystallization we prepared some tens of pure specimens of alum and of saltpetre which respectively had identical electrical conductivities and temperature dependences of the electrical conductivity.

The specific electrical conductivity σ can always be expressed as a product of the concentration n of current carriers, their charge e and their mobility u (defined as the average translation velocity along unit electric field)

$$\sigma = neu. \quad (1)$$

The current density j , equal to the ratio of the current J to the cross-section area S of the conductor, is given by

$$j = neu\mathcal{E} \quad (2)$$

where \mathcal{E} is the electric field.

A radioactive tracer technique now makes it possible to observe the average mobility of ion transfer along the field directly and thus to separate n and u in expression (1).

The mobility of ions in an electrical field can also be estimated from the diffusion coefficient D . Einstein established a universal relationship between D and u

$$\frac{D}{u} = \frac{kT}{e} \quad (3)$$

where k is Boltzmann's constant which is equal to 1.38×10^{-16} erg/degree. Most measurements of ion mobility were, however, carried out before radioactive tracers made their appearance, using indirect chemical methods.

The nature of the current carriers

The electrolytic nature of the current can be established by the liberation of the products of electrolysis at the electrodes, in quantities prescribed by Faraday's law. Errors may, however, occur due to secondary processes at the electrodes or at the boundary between two solid electrolytes forming an electrical circuit. The metal deposited at the cathode often forms sharp needles, dendrites, of low resistivity, penetrating into the crystal. These internal metallic needles become electrodes at which the products of electrolysis are liberated. This may

lead to an appreciable source of error in the subsequent weighing of the electrode. When such needles reach the anode they become metallic bridges carrying the current and the electrolysis of the crystals ceases. It is, therefore, essential to eliminate the formation of dendrites at the cathode when carrying out such investigations.

The proof of the ionic character of the current becomes more convincing when the proportions of current transferred by each type of ion, both positive and negative, are measured. For this purpose the conductor is divided into three or more parts, each of which is weighed separately before the experiment and after the passage of current J during time t . The end portions are weighed together with the electrodes (Fig. 1).

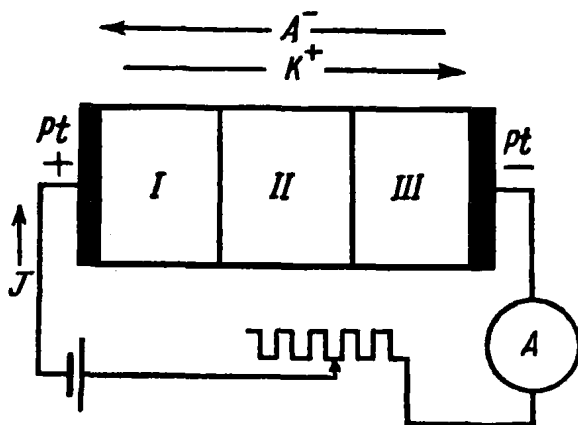


Fig. 1. An experiment for determining transfer numbers in solid electrolytes:
 A^- , anions; K^+ , cations; I, II, III, parts of the conductor.

When a quantity of electricity Q equal to Jt passes through the conductor, a corresponding amount of the substance is transferred by the ions. By determining the change of the weight of each of the three portions it is possible to estimate the amount of substance liberated by the current at each electrode and the proportion of positive and negative ions in the total current. Thus, for example, when the current is transferred only by positive ions an increase in weight corresponding to Faraday's law is observed in the portion adjoining the cathode which is equal to the loss in weight of the portion adjoining the anode.

Verification of Faraday's law and measurement of the ion transfer numbers can only be carried out with appreciable currents and, therefore, with a reasonably high electrical conductivity of the material. At low electrical conductivities, one has to be satisfied with indirect

symptoms in order to decide whether the current mechanism is ionic or electronic. The following criteria can be used:

1. Ionic conduction is indicated by electrical polarization at the electrodes which keeps the current virtually equal to zero up to a certain potential difference V_0 of the order of 1–2 V; when this is exceeded the current is proportional to $V - V_0$.

2. E.m.f.s may be set up in a conductor carrying a current in a magnetic field. When the magnetic field is perpendicular to the direction of the current, an additional electrical field perpendicular to the magnetic and electrical fields appears in electronic conductors (a transverse potential difference). When the current mechanism is ionic this phenomenon (the Hall effect) is not observable. Even in electronic conductors this field is sometimes so weak that it remains unnoticed.⁽¹⁾

3. The temperature dependence of the electrical conductivity makes it possible to estimate the energy required for the liberation and movement of the charges in the conductor. When this energy is the same at all temperatures and the electrolytic nature of the current has been established at high temperatures by the applicability of Faraday's law and the measurement of ion transfer numbers, then the current at low temperatures may also be attributed to ions. As a rule, however, the same dissociation energy is not applicable at high and low temperatures.

Cases of mixed ionic and electronic conductivity are not infrequent. Strict distinction between the two mechanisms often represents a complex problem requiring a thorough investigation of the behaviour of the materials over a wide temperature range.

How difficult it may sometimes be to establish the true character of current carriers is indicated by the example of the high-temperature modification of silver sulphide, Ag_2S .

In 1833, Faraday, studying the currents in Ag_2S , discovered that, in contrast to the behaviour of a metal, its electrical conductivity rises with temperature reaching values characteristic of the majority of metals at high temperatures. Twenty years later Hittorf reached the conclusion that $\alpha\text{-Ag}_2\text{S}$ is a solid electrolyte. Fifty years later $\alpha\text{-Ag}_2\text{S}$, together with other sulphides, was classified among metallic conductors.⁽²⁾

In 1920 Tubandt measured the Faraday constant and the transfer numbers for $\alpha\text{-Ag}_2\text{S}$ and found that all the current is transferred by silver ions. It seemed that the nature of conductivity of $\alpha\text{-Ag}_2\text{S}$ was definitely established.

There were, however, several signs pointing towards an electronic conduction mechanism:

1. The calculated ion mobilities based on Tubandt's hypothesis gave values exceeding those for all known solid electrolytes. The diffusion coefficient D was measured for $\alpha\text{-Ag}_2\text{S}$ and related to the mobility u by

Einstein's law (expression (3)). The mobility calculated on the basis of the measured diffusion coefficient was 1000 times less than expected.

2. Klaiber observed an appreciable Hall effect which is a sure sign of electronic conduction.

3. The e.m.f. of a galvanic element made of platinum, sulphur, α -Ag₂S and silver was found to be equal to a few thousandths of a volt as compared with 0.2 V expected from an electrolytic cell.

Finally, in 1933 Wagner proved that an error had crept into Tubandt's experiments; the liberation of silver and sulphur was not due to electrolysis but to diffusion of silver atoms through silver sulphide, the atoms forming silver sulphide at the sulphur boundary.

One can now consider it to be definitely established that the currents in the high-temperature modification of silver sulphide are electronic and the part played by ionic conduction, if it takes place at all, does not exceed 1%.

The current mechanism in solid electrolytes

At low temperatures each ion is fixed in the crystal lattice in a position corresponding to the minimum potential energy. In order to transfer the ion from this position into a new one so that it can move in the direction of the electrical field it is necessary to expend a certain amount of energy, called the dissociation energy ϵ . This energy may be provided by an appropriate fluctuation of its thermal motion. When an ion may exist in one of two states, the energies of which differ by ϵ , the ratio of the time it stays in the higher energy state to that in the lower energy state is given by the expression $\exp(-\epsilon/kT)$, where k is the Boltzmann's constant and T the absolute temperature.

Denoting by N the total number of ions per unit volume which may dissociate with an energy change ϵ , and the equilibrium number of dissociated ions which can participate in electrical conduction by N_i , we can calculate N_i approximately in the following way.

The number of ions which dissociate per unit time is

$$p = \alpha N \exp(-\epsilon/kT). \quad (4)$$

The number of ions which recombine in unit time is

$$z = \beta N_i \frac{N_i}{N}. \quad (5)$$

From the equilibrium condition we have $p = z$, whence

$$N_i = \sqrt{\left(\frac{\alpha}{\beta}\right)} N \exp(-\epsilon/2kT). \quad (6)$$

The dissociated ions move from positions, corresponding to the minimum of their free energy in the crystal lattice, into new positions (e.g. into spaces in the crystal cell between adjacent ions). The potential energy there is ϵ eV higher than the energy which they possess when occupying a lattice site (Fig. 2).

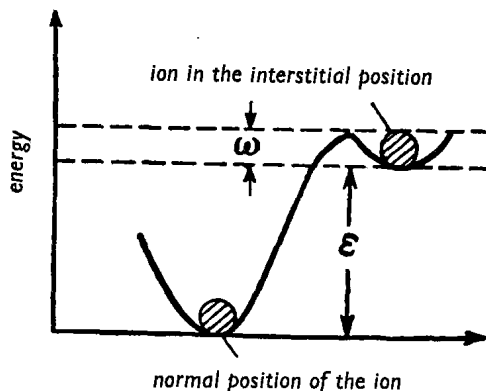


Fig. 2. Change of the potential energy of an ion on transition into an interstitial site of the crystal lattice (formation of defects according to Frenkel').

Similar positions with the same energy also exist in adjacent cells. In order to pass from one cell into another and to contribute in this way to the current, the ion must overcome a certain energy barrier each time, penetrating structural elements of the solid and then passing through intermediate positions where its energy will be higher by ω eV. This additional energy is picked up by the ion from the thermal vibrations.

Under the effect of thermal agitation a dissociated interstitial ion undergoes a continuous oscillation with a frequency ν depending on the forces acting on it. The ion therefore approaches the barrier, of height ω eV, ν times per sec. The probability that in one of these attempts it will succeed in overcoming the barrier, raising its energy by ω eV, is given by the expression derived from statistical physics

$$\exp(-\omega/kT). \quad (7)$$

It is therefore expected that in unit time the ion will pass $\nu \exp(-\omega/kT)$ times from cell to cell, diffusing through the crystal until it reaches a vacant lattice site where an ion of the same sign is absent, or until it attaches itself to a crystal defect with a lower energy than that on an interstitial site.

The energy ω received by the ion in overcoming the barrier is carried over in the form of increased oscillations as the ion passes into

a new cell. When the amplitude of the oscillation decreases, the ion gives up its surplus energy ω to the surrounding atoms in the form of thermal energy.

When ω is small in comparison with ϵ , an ion which has left the equilibrium position at the lattice site will diffuse from one cell into another, moving equally often to the left and to the right, forwards and backwards, and upwards and downwards.

When an electrical field \mathcal{E} directed e.g. from left to right, exists in the crystal, all the positive ions will begin to move more frequently in this direction than in the opposite direction, whilst the negative ions will be assisted by the field in moving from the right to the left. It may be assumed that the predominance of transition in the direction in which the field acts over the opposite direction will on an average be proportional to the field strength \mathcal{E} . The average distance covered by an ion in one second in the direction of the field or its average velocity may be expressed as a product of the total number of transitions $\nu \exp(-\omega/kT)$ and the probability of transition in the direction of the field, which is proportional to \mathcal{E} , and will be denoted by $\gamma\mathcal{E}$. We have, therefore,

$$v = \gamma\mathcal{E}\nu \exp(-\omega/kT)$$

and the mobility u_i , or average translation velocity in unit field is

$$u_i = \gamma\nu \exp(-\omega/kT).$$

The electrical conductivity σ , according to expression (1) can be written either as

$$\sigma_i = e \frac{\alpha\gamma\nu N_i}{\beta_1} \exp\left(-\frac{\omega + \epsilon}{kT}\right), \quad (8)$$

when there is a large number of defects to which the ions may attach themselves, or as

$$\sigma_i = e\gamma\nu \sqrt{\left(\frac{\alpha}{\beta_2}\right)} N_i^{\frac{1}{2}} \exp\left(-\frac{\epsilon + 2\omega}{2kT}\right), \quad (8a)$$

when the ions recombine with empty lattice sites.

After the crystal has been maintained at temperature T for a sufficiently long time, an equilibrium will be established under which the ions will become distributed in the most probable way between their (a) normal positions in crystal lattice sites, (b) cracks and defects, and (c) interstitial sites with increased energy ϵ . Similarly, a stationary distribution independent of time will be set up in an electric field \mathcal{E} . As long as Ohm's law is valid it ought to be considered that the electrical field \mathcal{E} does not appreciably change the equilibrium distribution and, therefore, the concentration of the free ions.