

*Electrical Conduction
in Solid Materials*

SUCHET

ELECTRICAL CONDUCTION IN SOLID MATERIALS

(Physicochemical Bases and Possible Applications)

BY

J. P. SUCHET

*Université René Descartes, Centre Luxembourg,
F-75270 PARIS CEDEX 06*



PERGAMON PRESS

OXFORD • NEW YORK • TORONTO • SYDNEY • BRAUNSCHWEIG

PERGAMON PRESS LTD.,
Headington Hill Hall, Oxford
PERGAMON PRESS INC.,
Maxwell House, Fairview Park, Elmsford, New York 10523
PERGAMON OF CANADA LTD.,
207 Queen's Quay West, Toronto 1
PERGAMON PRESS (AUST.) PTY. LTD.,
19a Boundary Street, Rushcutters Bay, N.S.W. 2011, Australia
PERGAMON PRESS GmbH,
Burgplatz 1, Braunschweig 3300, West Germany

Copyright © 1975 J. P. Suchet

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of Pergamon Press Ltd.

First edition 1975

Library of Congress Cataloging in Publication Data

Suchet, Jacques Paul, 1923—

Electrical conduction in solid materials.

(International series of monographs in the science of the solid state; v. 9)

Includes bibliographies and indexes.

1. Semiconductors. 2. Solids—Electric properties

I. Title.

QC611.S933 1974 537.6'22 74-19450

ISBN 0-08-018052-3

Printed in Great Britain by A. Wheaton & Co., Exeter

**INTERNATIONAL SERIES OF MONOGRAPHS IN
THE SCIENCE OF THE SOLID STATE**

GENERAL EDITOR: B. R. PAMPLIN

VOLUME 9

**ELECTRICAL CONDUCTION
IN SOLID MATERIALS**

(Physicochemical Bases and Possible Applications)

Suchet, so werdet ihr finden.

(Seek and ye shall find.)

(Lukas xi. 9)

v. 9)

By the Same Author

Les Varistances et leur emploi dans l'électronique moderne (The Varistors and Their Use in Modern Electronics) (in French), Chiron, Paris, 1955.

Chimie physique des semiconducteurs (Physical Chemistry of Semiconductors) (in French), Dunod, Paris, 1962; Russian translation, Izd. Metallurgiya, Moscow, 1964.

Id. (enlarged manuscript); English translation, van Nostrand, London, 1965; Polish translation, PWN, Warsaw, 1966.

Id. (again enlarged manuscript); Russian translation (2nd edn.), Izd. Metallurgiya, Moscow, 1969.

Curso de compostos químicos semicondutores (Course on Chemical Semiconducting Compounds) (in French), Centro Técnico de Aeronautica, São José dos Campos, SP, Brazil, 1963.

Crystal Chemistry and Semiconduction in Transition Metal Binary Compounds, Academic Press, New York, 1971.

Edited by the Author

Séminaires de chimie de l'état solide (Seminars on Solid State Chemistry), yearly publication (in French):

1. *Liaisons interatomiques et propriétés physiques des composés minéraux (Interatomic Bonds and Physical Properties of Inorganic Compounds)*, SEDES, Paris, 1969.
2. *Croissance de composés minéraux monocristallins (Growth of Monocrystalline Inorganic Compounds)*, Masson, Paris, 1969; Russian translation, Izd. Metallurgiya, Moscow, 1970.
3. *Influence des changements de phase sur les propriétés physiques des composés minéraux (Influence of the Phase Changes on the Physical Properties of the Inorganic Compounds)*, Masson, Paris, 1970.
4. *Appareillages et techniques de caractérisation des composés minéraux solides (Apparatus and Techniques of Characterization of the Solid Inorganic Compounds)*, Masson, Paris, 1971.
5. *Quelques aspects de l'état solide organique (Some Aspects of the Organic Solid State)*, Masson, Paris, 1972.
6. *Diagrammes de phases et stoechiométrie (Phase Diagrams and Stoichiometry)*, Masson, Paris, 1973.
7. *L'Infrarouge en chimie des solides (The Infrared in Chemistry of Solids)*, Masson, Paris, 1974.
8. *Les Solides divisés et dispersés (The Divided and Dispersed Solids)*, Masson, Paris, 1974.
9. *Couches minces, émaux et vernis (Thin Layers, Enamels and Varnishes)*, in preparation.
10. *Bilan et perspectives en chimie des solides (Review and Prospects in Chemistry of Solids)*, in preparation.

Preface

THE local section of the Société Chimique de France, at the suggestion of Professor Aubry, invited me to deliver a lecture on 25 May 1972 at Nancy University entitled "Electrical conductivity in the solid state and its applications". I realized the scale of the subject on that occasion, and had regretted that the limited time at my disposal allowed me to give only a very rapid summary of the question.

Shortly afterwards, the Convention Intercantonale Romande pour l'Enseignement du 3^{ème} Cycle en Chimie, at the suggestion of Professor Feschottes, invited me to give a course in Lausanne University, in February and March 1973, consisting of six lectures on "Semiconductor materials". This provided me with the opportunity I had wanted to deal in greater detail with conventional, magnetic, and switching semiconductor materials, and their various applications.

I then suggested to my friend Brian Pamplin that I should write up my notes, complete them by dealing also with conducting and insulating materials and their applications, and publish it all in the series "The Science of the Solid State", to provide students, teachers, and engineers—mainly those with chemical or metallurgical training—with a straightforward work linking the properties of such materials closely with their applications.

While British students often receive a balanced education as physico-chemists, this does not apply on the Continent, particularly in Germany, France, and Italy, where physics and chemistry are usually separated. Far too many physicists are thereby directed towards theoretical research, and many need retraining to be of any use in industry. This book will provide such students with a wider-ranging, simpler viewpoint than a treatise of strictly physical theory, the field of application of which is still so restricted.

As for an earlier work, the English text has been prepared in collaboration with Denis Mahaffey.

Paris

J. P. SUCHET

Contents

Preface	xi
---------	----

Part I PHYSICOCHEMICAL BASES

<i>Chapter 1</i> Conductors	3
1.1 Interatomic bonds	3
1.2 Conductors and semiconductors	7
1.3 Metals and alloys	9
1.4 Magnetic conductors	12
1.5 Resistance at low temperatures	17
References	20
<i>Chapter 2</i> Conventional Semiconductors	22
2.1 Intrinsic semiconductors	22
2.2 First condition	26
2.3 Binary and ternary compounds	29
2.4 Second condition	32
2.5 Effective atomic charge	35
References	39
<i>Chapter 3</i> Magnetic Semiconductors	40
3.1 Roles of s, p, and d electrons	40
3.2 d transfers and chemical bond	44
3.3 Simple binary compounds	48
3.4 Compounds with the NiAs structure	51
3.5 Ternary compounds	55
References	59
<i>Chapter 4</i> Switching Semiconductors	60
4.1 Magnetic transitions	60
4.2 Crystallographic transitions	64
4.3 Chalcogenide glasses	67
4.4 Reversible crystallization	69

CONTENTS

4.5 Non-destructive breakdown	73
References	76
<i>Chapter 5 Insulators</i>	78
5.1 Inorganic insulators	78
5.2 Organic insulators	82
5.3 Alternating currents	85
5.4 Dielectrics	90
5.5 Ferroelectrics	93
References	96
<i>Part II POSSIBLE APPLICATIONS</i>					
<i>Chapter 6 Conductors</i>	99
6.1 Electricity lines	99
6.2 Telecommunications by wire	102
6.3 Magnetic coils	105
6.4 Resistors and couples	109
6.5 Contact parts	113
References	116
<i>Chapter 7 Conventional Semiconductors</i>	118
7.1 Extrinsic semiconductors	118
7.2 P-N junction: photocell, rectifier	122
7.3 Multiple junction: amplifier	125
7.4 Heterojunction: thermocell	129
7.5 Other applications	132
References	136
<i>Chapter 8 Magnetic Semiconductors</i>	137
8.1 Thermistors	137
8.2 Magnetoresistance commutator	140
8.3 Special magnetoelectric effects	144
8.4 Magneto-optical effects	147
8.5 Laser modulator	151
References	155

<i>Chapter 9</i>	Switching Semiconductors	156
9.1	Thermal detector	156
9.2	Memory switch	158
9.3	Threshold switch	161
9.4	Special glass IRdome	164
9.5	Other applications of glasses	166
	References	169
<i>Chapter 10</i>	Insulators	171
10.1	Electrotechnical insulator	171
10.2	Electromechanical resonator	175
10.3	Condenser, amplifier	178
10.4	Light modulator	181
10.5	Memory, electret	185
	References	187
	Guide to Recent Books	189
	Author Index	199
	Subject Index	205
	Formula Index	211

Part I

Physicochemical Bases

Chapter 1

Conductors

1.1. Interatomic bonds

A solid phase contains a very large number of atoms, all identical in the case of an element, or of several different kinds in the case of an alloy or chemical compound. These atoms are linked with one another by means of their electrons on which cohesion of the solid depends. But these bonds can be of several different types, depending a great deal on the total ionization energies of the atoms present, in other words the energies needed to move all the valency electrons of these atoms to infinity. For an atom of a given element, the term of this operation is a positively charged ion, the electronic formula of which is that of the rare gas preceding the element in the Periodic Table of Elements. Table 1.1 gives these energies in electron volts for the main elements.

Atoms for elements which have low numbers (less than about 35) on this table combine with one another in the form of compact stacks of spheres, and part of their valency electrons escapes from the attraction of their nuclei, forming a gas of delocalized electrons ready to move in an electric field. This is the *metallic bond*, to be found in metals and alloys, where it gives rise to chemical formulae, the lower indices of which are usually neither simple nor unique for a given association of elements. Electrical conduction of phases with this type of bond is naturally high, and entirely due to the delocalized electron gas.

When one solid phase contains atoms of elements for which the numbers in Table 1.1 are in some cases lower and in other cases higher than 35, atoms in elements with numbers above 35 do not lose their electrons but tend to complete their electronic valency octet at the expense of atoms of elements with numbers below 35, thus attaining the

Table 1.1. BASED ON SUCHET, 1962

Li 5.4			Be 18.1		B 37.7	C 64.2	N 97.4	O 137	F 184
Na 5.1			Mg 15.0	Al 28.3	Si 44.9	P 64.7	S 87.6	Cl ?	
K 4.3	Cu 7.7	Ca 11.8	Zn 18.0	Ga 30.6	Ge 45.5	As 62.5	Se ?	Br ?	
Rb 4.2	Ag 7.5	Sr 11.0	Cd 16.8	In 27.9	Sn 39.4	Sb 55.5	Te (72)	I ?	
Cs 3.9	Au 9.2	Ba 9.9	Hg 18.6	Tl 29.7	Pb 42.1	Bi 55.7			

0 5 10 15 25 35 50 70 eV

electronic formula of the rare gas following them in the Periodic Table of Elements. They therefore associate simply with one another, in accordance with known valency rules, in the form of stacks of charged spheres (cations and anions), at a distance such that their mutual attraction balances the repulsion of their electronic clouds. This is the *ionic bond*, to be found in many chemical compounds for which the formulae use low sub-indices, depending only on the columns of the classification table to which their elements belong. All the electrons are retained by the nuclei if the arrangement is perfectly regular; and electrical conduction is accordingly nil at very low temperatures.

This image of rigid spheres, however, soon proves false when the atomic number of the elements rises, together with the dimensions of the atom. Large ions can be deformed in the electric field created by their neighbours. The spherical symmetry of the electronic cloud of the atom is then no longer respected, and a dipole is induced inside the cloud. The electrical field responsible for this *polarization* of large ions is mainly due to highly charged small ions (cations). Table 1.2 shows the ratio of the number of elementary charges n carried by the cation to its ionic radius r for the main elements. This ratio is to some extent a measurement of the variation in relation to a pure ionic bond.

Let us assume that elements such as carbon, sulphur, or selenium are involved. Identical atoms cannot associate here by means of metallic bonds since the total ionization energies shown in Table 1.1 are too high. But they cannot associate either by means of an ionic bond since the n/r ratios shown in Table 1.2 are very high, and the very high polarization of the anions C^{4-} , S^{2-} , or Se^{2-} would immediately destroy such a bond. So what happens? The electronic clouds interpenetrate in the directions in which the cation field would be strongest, each atom pooling one electron in this direction with its neighbour. This is the *covalent bond*, the distinctive feature of which is accordingly its directional character.

In this pooling process, then, an atom cannot gain more electrons than it had to start with, and only atoms of elements in columns IV, V, VI, and VII of the Periodic Table can thus complete their octet by forming four shared electronic pairs per atom (tetrahedral structure of carbon atoms in the diamond), three pairs per atom (trigonal structure of phosphorus or arsenic atoms), two pairs per atom (right-angled

ELECTRICAL CONDUCTION IN SOLID MATERIALS

spirated chain for selenium), or one pair per atom (Cl_2 molecules). All the electrons are either retained by the nuclei, as in an ionic bond, or immobilized in shared pairs, so that electrical conduction is still nil at very low temperatures.

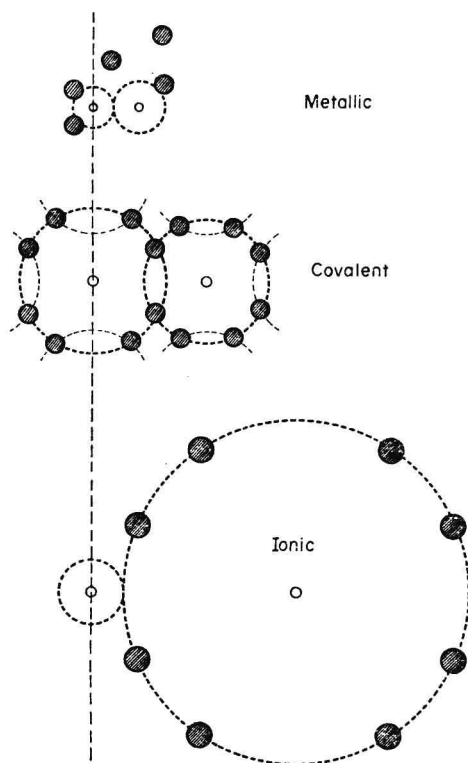


FIG. 1.1. Schema of the different types of interatomic bonds (based on Suchet, 1962).

The various types of bonds described above are shown in diagrammatical form in Fig. 1.1. For atoms of comparable mass, the interatomic distance increases as one passes from the metallic bond to the covalent bond, and then to the ionic bond.

1.2. Conductors and semiconductors

What happens to the electrical conduction if the field of very low temperatures is abandoned and the solid allowed to heat up? The effect of temperature on the electron gas mentioned in connection with the metallic bond is not very great, and *electronic conduction* accordingly remains largely unchanged. Let us leave aside the field of very low and low temperatures, to which we shall return in subsequent sections. A very simple, more or less linear, relation can be observed between conductivity σ and the centesimal temperature t :

$$\sigma \sim \sigma_0(1 - 0.004t),$$

where σ_0 is the conductivity at 0°C . The negative sign of the coefficient of t is explained by the thermal agitation of the atoms, which offers increasing opposition to the movements of free electrons. At room temperature, values range from around 5×10^5 mhos/cm for noble metals (Ag, Al, Au, Cu) to 10^4 mhos/cm for bismuth, with even lower figures for some transition metals such as manganese or lanthanides such as gadolinium.

In the case of a highly ionic bond, electrons remain attached to the nuclei until high temperatures are reached, and the solid is thus insulating. For instance, the conductivity of quartz SiO_2 is only 10^{-17} mhos/cm at room temperature. The diffusion coefficient of an element may, however, be sufficiently high in a compound, e.g. if the compound crystallizes in a defect structure for movements of ions to be possible. Very low conduction then appears, known as *ionic semiconduction*, which is always accompanied by electrolysis phenomena in the neighbourhood of the electrodes supplying the current, since material is being conveyed.* In the case of a covalent bond, elements with low atomic weights and their compounds remain insulating for a fairly long time, such as sulphur with only 10^{-16} mhos/cm and BN with 10^{-10} mhos/cm at room temperature. On the other hand, if there are elements with high atomic weight, breaking of some bonds is easier when temperature rises, releasing electrons that can conduct the electric current. This particular conduction, less than in metallic conduction, is known

* This phenomenon may be considered as an extension of the ionic conduction in *liquid* materials and, for this reason, will not be discussed in this book.