PRINCIPLES OF THE SOLID STATE

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Preface

Scientists, engineers and technologists alike are interested in materials with tailor-made characteristics. Chemists and physicists provide a base over which the edifices of Materials Science, Engineering and Technology have been built up. Despite the availability of several excellent books on Solid State Chemistry and Solid State Physics, the need for a concise treatise embodying the principles of solid state science is increasingly being felt. Hence an attempt has been made to present an integrated, scientists' approach, which hopefully will appeal to students of both chemistry and physics.

The book is primarily intended for B.Sc., M.Sc. (Part I) and Engineering students, although its material could also serve as a refresher course for research scholars and practising scientists. An emphasis has been laid on the principles governing the synthesis, structure and physical properties of crystalline solids. Specific materials have been discussed only to illustrate the application of the principles. The treatment is non-mathematical; however, wherever unavoidable, elementary methods involving determinants, matrices and differential equations have been employed. An extensive use of quantum mechanics has been avoided in order to make the text meaningful to a broad spectrum of readers.

The book begins with an introduction to bonding and structure; structural aspects have been confined to identification of lattice/structure, rigorous crystallography being omitted. This is followed by discussion of physical properties such as thermal, electrical, magnetic, optical and dielectric. The synthetic aspect involves solid state reactions and single crystal growth techniques, which is preceded by consideration of various types of imperfections. A number of representative problems have been given at the end of each chapter to serve as a study-aid. Appendices have been provided to make the treatment self-sufficient.

Several research journals and excellent textbooks have greatly influenced the material and methodology adopted in the text. These are listed in Appendices C and D respectively. My students have also contributed immensely by insisting on adequate explanations.

The author is greatful to all the publishers and authors for their permission to reproduce and/or modify figures and/or tables. John Wiley and Sons., Inc., should be mentioned in particular. The author is also thankful to Professors Charles Kittel, L. V. Azaroff, J. M. Honig, C. N. R. Rao, E. S. R. Gopal, A. P. B. Sinha and P. Krishna for their cooperation and help.

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The material presented in the text is the result of lecture notes compiled over a decade. In spite of the best efforts to keep track of original sources from which the material and/or idea(s) were borrowed, there could be some lapses, which alert reader

may recognise. They are requested to intimate to the author so that due acknowledgement of the source(s) could be made. In the meantime, the concerned author/publishers should forgive for the lapse(s).

Comments and suggestions to improve upon the text are most welcome.

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	W.G. Moffatt, G.W. Pearsall and J. Wulff, 'Structure'.	1964	Figs. 2.1, 2.2, 2.7, 2.8, 2.9, 2.18
	J.H. Brophy, R.M. Rose and J. Wulff, 'Thermodynamics of Structure'.	1966	Table 7.3, Fig. 7.16
	R.M. Rose, L.A. Shepard and J. Wulff, 'Electronic Properties'.	1966	Fig. 7.25
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McGraw-Hill Publishing Company	L.V. Azaroff and M.J. Buerger, 'Powder Method in X-ray Crystallography'.	1958	Figs. 1.8, 1.9, 1.10
	C.A. Wert and R.M. Thomson, 'Physics of Solids'.	1964	Figs. 2.12, 2.13, 2.23
	L.V. Azaroff and J.J. Brophy, 'Electronic Processes in Materials'.	1963	Figs. 6.2, 6.3, 6.5, 6.8, 6.9, 6.10, 6.16, 6.28
Prentice-Hall, Inc.	N.B. Hannay, 'Solid State Chemistry'.	1967	Figs. 2.6, 2.14, 2.19(b), 2.22, Q. 7.1 Fig. 1, 7.15, 7.18, 7.33.
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Mir Publishers	E.I. Epifanov, 'Solid State Physics'.	1979	Figs. 2.15, 2.24, 2.25
	V. Bruk, V. Garshenin and A. Kurnosov, 'Semiconductor Technology'.	1969	Fig. 7.31
Oxford University Press	H.M.Rosenberg, 'The Solid State'.	1975	Q. 6.7, Fig. 1
E.S.R. Gopal	Bull. Mater. Sci., **3**, (1981) 91.	1981	Fig. 7.14
D.B. McWhan	D.B. McWhan and J.P. Remeika, Phys. Rev. **B2** (1970), 3734.	1970	Fig. 7.5
I. Tarjan and Akademiai Kiado	Eds. I. Tarjan and M. Matrai, 'Laboratory Manual on Crystal Growth', Akademiai Kiado, Budapest	1972	Figs. 7.26, 7.27, 7.28, 7.29, 7.30, 7.32, 7.34

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D.M. Adams	'Inorganic Solids', John Wiley and Sons, Inc. (1974)	Figs. 1.14, 1.15, 1.16, 1.17
John Wiley and Sons, Inc.	C. Kittel, 'Introduction to Solid State Physics', Third Edition (1966).	Figs. 2.3, 2.4, 2.5, 2.17, 2.19, 2.20, 2.26, 3.12, 3.13, 4.4, 4.16, 4.22, 4.23, 4.24, 4.26
	Fifth Edition (1976) W.G. Moffatt, G.W. Pearsall and J. Wulff, 'Structure' (1964).	Figs. 6.24, 6.27, Fig. 2.21
Academic Press and R.A. Levy	'Principles of Solid State Physics' Academic Press (1968).	Figs. 2.28, 2.29, 3.2, 3.4, 3.6, 3.7, 3.16, 4.1

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A.J. Dekker	'Solid State Physics', Prentice Hall (1957).	Fig. 4.5
L.V. Azaroff and J.J. Brophy	'Electronic Processes in Materials' McGraw-Hill, Inc. (1963)	Figs. 4.6, 4.21, 6.6
S. Chandra	'Superionic Solids', North-Holland (1981).	Fig. 4.39 (b)
A. Earnshaw	'Introduction to Magneto-chemistry', Academic Press (1968)	Fig. 5.5
J.C. Slater	Cited in L.V. Azaroff and J.J. Brophy, 'Electronic Processes in Materials', McGraw-Hill, Inc. (1963).	Q. 5.6, Fig. 1
P. Goldberg (Ed.)	'Luminescence of Inorganic Solids', Academic Press (1966).	Tables 6.1, 6.2, 6.3. Figs. 6.17, 6.21, 6.22
J.C. Anderson	'Magnetism and Magnetic Materials' Chapman and Hall (1968).	Fig. 5.14
L.V. Azaroff	'Introduction to Solids', McGraw-Hill, Inc. (1960).	Fig. 6.12
G. Rupprecht and R.O. Bell	Phys. Rev., **135** (1964) A 748.	Fig. 6.30
John-Wiley and Sons, Inc. and P. Krishna	A.R. Verma and P. Krishna, 'Polymorphism and Polytypisum in Crystals' (1966)	Fig. 7.1 Table 7.1
H.C. Casey, Jr. and M.B. Panish	'Heterostructure Lasers', Academic, New York (1978).	Q. 6.5 Fig. 2(a)
W.J. Merz	Phys. Rev. **76** (1949) 1221.	Fig. 7.2
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Pergamon Press and H. Reiss (Ed.)	'Progress in Solid State Chemistry', Pergamon Press, Oxford (1964).	Part of Table 6.4
C. Sykes and H. Wilkinson	J. Inst. Metals, **61** (1937) 223.	Fig. 7.10
E.U. Condon and H. Odishaw (Eds.)	'Handbook of Physics', McGraw-Hill (1967)	Table 7.2
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John Wiley and Sons, Inc.	B. Chalmers, 'Physical Metallurgy' (1959).	Figs. 7.20, 7.21, 7.22, 7.23, 7.24
S.S. Sekhon and R. Kamal	Physics News, Vol. 8 (1977)	Table 7.5

LIST OF SYMBOLS/ABBREVIATIONS

ϕ	potential energy, lattice energy
r	interparticle distance, radius
α	polarizability, Madelung constant, Seebeck coefficient, thermal expansion coefficient
μ	dipole moment, mobility, electrochemical potential, magnetic permeability, micron
°C	degree Celsius
K	Kelvin, thermal-conductivity, phonon wave number, partition coefficient
σ	electrical conductivity, stress
k_B	Boltzmann constant
E_g	band gap
h, k, l	Miller indices
n	principal quantum number, density, refractive index
λ	wavelength, molecular field constant
I	intensity, current
θ_{hkl}	Bragg angle/glancing angle
d_{hkl}	interplanar distance/spacing
N_A	Avogadro's number
$\vec{k}$	wave vector
k	wave number
$\vec{G}$	reciprocal lattice vector
v	linear velocity
e	electronic charge, electron
Z_e	ionic charge
S	entropy, total spin
T	absolute temperature
P	pressure, polarisation
V	volume, periodic potential, voltage
β	compressibility coefficient
J	joule, current density, total angular momentum

C	coulomb, capacitance, heat capacity, concentration
Å	angstrom
m	metre, mass, magnetic quantum number
N	newton, total number
R	resistance, gas constant
l	length, mean free path, orbital momentum quantum number
ρ	electrical resistivity
m_e	rest mass of electron
τ	relaxation time/average collision time
h	Planck's constant
ψ	wave function
E	total energy
m^*	effective mass
ω	angular frequency
$f(E)$	Fermi-Dirac probability
$\mathcal{E}$	electric field
G	Gibbs free energy
E_F	Fermi energy/level
T_F	Fermi temperature
$S(E)$	density of available states
$N(E)$	density of occupied states
C_e	electronic heat capacity
p	density of holes
μ_n	electron mobility
μ_p	hole mobility
E_v	valence band edge
E_c	conduction band edge
n_0	effective density of states of electrons in the conduction band
p_0	effective density of states of holes in the valence band
ε_r	static dielectric constant
ε_0	electric permittivity of free space
N_d	total density of donor states
N_a	total density of acceptor states
N_d^0	density of unionized donor states

N_a^0	density of unionized acceptor states
N_d^+	density of ionized donor states
N_a^-	density of ionized acceptor states
E_d	energy of donor state
E_a	energy of acceptor state
E_D	separation between donor states and conduction band edge
H_c	coercive force, threshold magnetic field to destroy superconductivity
$\vec{B}$	magnetic flux density vector
θ_D	Debye temperature
D	diffusion coefficient, dielectric displacement
η	rate of jumps
ΔG^*	free energy of activation
r_p	effective radius of polaron
w	work function
ν_0	lattice vibration frequency
W	band width
U	intra-atomic coulomb repulsion
E_i	activation energy for diffusion
E_m	activation energy for migration
A	ampere, Helmholtz free energy
eV	electron volt
P_{O_2}	oxygen partial pressure
h	hole
m_l	magnetic quantum number
$\vec{L}$	orbital angular momentum
s	spin quantum number
$\vec{S}$	spin angular momentum vector
m_s	spin magnetic quantum number
$\vec{J}$	total angular momentum vector
j	total angular momentum quantum number
m_j	total magnetic quantum number
μ_0	magnetic permeability of free space
$\vec{H}$	magnetic field vector
H	magnetic field, enthalpy

μ_r	relative magnetic permeability
M	magnetic moment, magnetization
χ	magnetic susceptibility
μ_B	Bohr magneton
g	Lánde factor
ω_L	Larmor (angular) frequency
T_c	Curie temperature, transition temperature
T_N	Néel temperature
T_{FN}	ferrimagnetic Néel temperature
Wb	weber
B	Brillouin function
μ_{eff}	effective Bohr magneton number
Δ_{ex}	exchange energy
Δ	crystal field splitting
H_i	internal magnetic field
n_{eff}	effective number of Bohr magnetons (per atom)
E_{ex}	exchange energy
J_{ex}	exchange integral
ν	linear frequency
χ_e	static (di)electric susceptibility
ε	electric permittivity
χ_e^*	complex electric susceptibility
ε_r^*	complex dielectric constant

CONTENTS

1

BONDING AND STRUCTURE

1.1 TYPES OF MATTER

Since the ancient times, solid materials have played a vital role in the progress of mankind. While the stone-age caveman used sharp stones as weapons, subsequent iron age heralded the emergence of metals as the key materials. In those times, properties of naturally available materials were discovered by trial and error and the materials were put to use profitably. With the passage of time, this trial and error method gave way to the choice and selection of materials, once man realized that properties could be designed and materials with tailor-made characteristics could be synthesized. Today, the science and technology of materials is in such an advanced stage as to allow the application of physico-chemical principles for the design of desired new materials in ceramic, single crystal and/or amorphous forms. Semiconductors, ferrites, magnetic garnets, solid state lasers, piezoelectrics, ferroelectrics, ultraviolet- and infrared-sensitive crystals, magnetic bubbles, etc., are a part of the several solid state devices in use to-day. This advancement of science and technology of solids is mainly due to the awareness that structure and properties are related at the 'molecular' level. The links between chemical bonding, structure, imperfections and properties—mainly electronic—are shown in Fig. 1.1 (a). Figure 1.1 (b) presents a bird's eye-view of the applications of solids in various spheres.

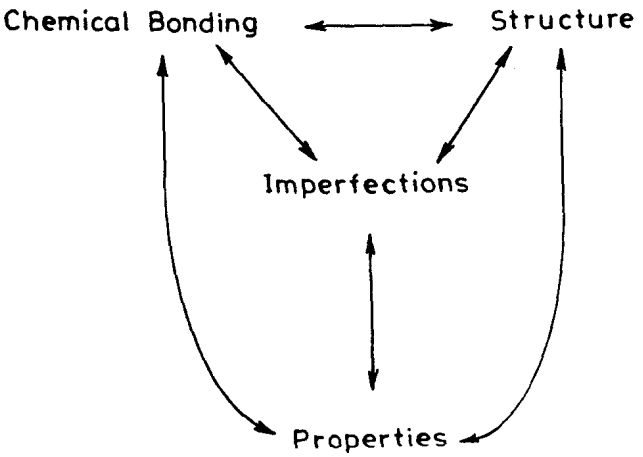

Fig. 1.1 (a) Interrelations of chemical bonding, structure, imperfections and properties of solids.