

# Contents

<b>1. Introduction</b> .....	1
<b>2. Introduction to Electronic States in Oxides and an Overview of Transport Properties</b> .....	5
2.1 Atoms in a Ligand Field .....	5
2.2 Electronic Energy Bands .....	10
2.3 Electron–Electron Interaction .....	10
2.3.1 Direct Interaction .....	10
2.3.2 Indirect Interaction .....	11
2.4 Electron–Phonon Interaction .....	11
2.4.1 The Adiabatic Approximation .....	11
2.4.2 The Fröhlich Model, the Deformation Potential and the Simple Metal .....	12
2.4.3 Polarons .....	13
2.5 Randomness .....	15
2.5.1 Anderson Localization .....	15
2.5.2 Variable Range Hopping .....	15
2.6 The Seebeck Coefficient and Hall Mobility .....	16
2.7 Magnetic Susceptibility .....	17
2.8 Metal–Insulator Transition (MIT) .....	19
2.9 Good Conductors .....	38
2.9.1 The NaCl Structure .....	40
2.9.2 The Corundum Structure .....	44
2.9.3 The Rutile Structure .....	45
2.9.4 The Perovskite Structure .....	47
2.9.5 The $K_2NiF_4$ Structure .....	52
2.9.6 $ReO_3$ and $M_xWO_3$ .....	52
2.9.7 Pyrochlores $A_2B_2O_{7-x}$ .....	53
2.9.8 Spinel .....	54
2.9.9 Low-Dimensional Oxides .....	55

<b>3. Theories for Many-Electron Systems with Strong Electron–Phonon and Interelectron Coulombic Interactions</b> . . . . .	57
3.1 Single-Body Problems	
in Strongly Coupled Electron–Phonon Systems . . . . .	60
3.1.1 Electrons, Phonons and Their Couplings . . . . .	60
3.1.2 Weak Coupling and Large Polarons . . . . .	61
3.1.3 Strong Coupling, Self-Trapping, Broken Symmetry and Dimensionality . . . . .	62
3.1.4 Dynamics of Self-Trapping . . . . .	65
3.2 Two-Body Problems	
in Strongly Coupled Electron–Phonon Systems . . . . .	67
3.2.1 Bipolarons . . . . .	67
3.2.2 Charge Separation of Self-Trapped Exciton . . . . .	69
3.3 Excitons and Solitons	
in One-Dimensional Charge Density Wave States . . . . .	71
3.3.1 Phase Diagram of the Ground State . . . . .	74
3.3.2 Nonlinear Lattice Relaxation and Proliferations of Excitons in One-Dimensional CDW . . . . .	76
3.3.3 One-Dimensional Extended Peierls–Hubbard Model . . . . .	78
3.3.4 Relaxation in One-Dimensional CDW . . . . .	80
3.4 Direct and Indirect Excitons	
in Three-Dimensional CDW State . . . . .	83
3.4.1 Three-Dimensional Extended Peierls–Hubbard Model for BaBiO <sub>3</sub> . . . . .	85
3.4.2 Direct and Indirect Excitons . . . . .	85
3.5 Competition Between Superconductivity and CDW State . . . . .	87
3.5.1 The Many-Polaron System . . . . .	88
3.5.2 Phase Diagram . . . . .	90
3.6 Superconducting Transition Temperatures of Strongly Coupled Electron–Phonon Systems . . . . .	94
3.6.1 Expected Behaviour of $T_c$ . . . . .	94
3.6.2 Interpolating Theory for $T_c$ by CPA . . . . .	95
3.7 Many-Electron System Coupling Strongly with Nonlinear Phonons . . . . .	98
3.7.1 BCS Limit, Nonlinear Phonons and Isotope Effects . . . . .	98
3.7.2 Anharmonic Peierls–Hubbard Model . . . . .	100
3.7.3 Anharmonicity and Metal–Insulator (CDW, SDW) Transitions . . . . .	101
3.7.4 Isotope Effects and Anharmonicity by the BCS Theory . . . . .	104
3.7.5 Migdal–Eliashberg Theory . . . . .	105
3.8 Non-Grassmann Path Integral Theory for Long-Range Coulomb Repulsion . . . . .	107

3.8.1	Quadratic Form for Long-Range Coulomb Interaction .	108
3.8.2	Path-Integral for Both Short- and Long-Range Parts . .	109
3.8.3	One-Body Green's Function Free from Grassmann Algebra . . . . .	110
3.8.4	Time-Dependent Bloch–De Dominicis Theorem . . . . .	113
3.8.5	Light Absorption Spectrum of the SDW State . . . . .	116
<b>4.</b>	<b>Electron–Electron Interaction and Electron Correlation . . . . .</b>	<b>119</b>
4.1	Introduction . . . . .	119
4.2	Microscopic Models of Interacting Electrons . . . . .	120
4.3	One-Electron Theories and Electron Correlation . . . . .	123
4.3.1	Hartree–Fock Approximation . . . . .	124
4.3.2	Local Density Approximation . . . . .	126
4.3.3	Electron Correlation Effects . . . . .	126
4.4	Electronic Structure of Transition-Metal Ions . . . . .	127
4.4.1	Hartree–Fock Scheme . . . . .	127
4.4.2	Ligand-Field Theory . . . . .	128
4.4.3	<i>d</i> Bands and Carrier Doping in Mott Insulators . . . . .	131
4.5	Hybridization Between <i>d</i> and <i>p</i> Electrons . . . . .	133
4.5.1	Mott–Hubbard Type and Charge-Transfer Type . . . . .	133
4.5.2	Configuration-Interaction Theory . . . . .	136
4.6	Magnetic Interactions . . . . .	140
4.6.1	Superexchange Interaction . . . . .	140
4.6.2	Local Moment in Metals . . . . .	142
4.7	Correlated Metals . . . . .	144
4.7.1	Metal–Insulator Transition . . . . .	144
4.7.2	Hubbard Model . . . . .	145
4.7.3	Fermi-Liquid Properties . . . . .	146
4.7.4	Long-Range Coulomb Interaction . . . . .	150
4.7.5	Mixed Valence States . . . . .	151
4.7.6	Anderson Localization . . . . .	152
<b>5.</b>	<b>Representative Conducting Oxides . . . . .</b>	<b>157</b>
5.1	ReO <sub>3</sub> : The Most Conductive <i>dε</i> Conductor . . . . .	158
5.1.1	Crystal Structure . . . . .	158
5.1.2	Electronic Properties . . . . .	160
5.2	SnO <sub>2</sub> and TiO <sub>2</sub> : Oxide Semiconductors . . . . .	168
5.2.1	Electronic Energy Band Structure of SnO <sub>2</sub> . . . . .	169
5.2.2	Electrical Conductivity of SnO <sub>2</sub> . . . . .	170
5.2.3	Optical Properties of SnO <sub>2</sub> . . . . .	175
5.2.4	TiO <sub>2</sub> . . . . .	177
5.3	LiTi <sub>2</sub> O <sub>4</sub> and LiV <sub>2</sub> O <sub>4</sub> : Weak-Coupling Superconductor and Temperature-Dependent Magnetism . . . . .	181

5.3.1	Crystal Structure . . . . .	182
5.3.2	Electronic Properties . . . . .	183
5.3.3	Superconducting Properties . . . . .	185
5.3.4	Insulating Properties: Nonzero Density of States . . . . .	186
5.3.5	$\text{LiV}_2\text{O}_4\text{-ZnV}_2\text{O}_4$ . . . . .	190
5.4	$\text{WO}_3$ and $M_x\text{WO}_3$ : Large Polarons . . . . .	191
5.4.1	Structure . . . . .	192
5.4.2	Electronic Properties in the Insulating Range and the Metal–Insulator Transition . . . . .	193
5.4.3	Superconductivity and Screening of the Electron–Phonon Interaction . . . . .	198
5.5	$M_x\text{V}_2\text{O}_5$ and $M_x\text{MoO}_3$ : Low-Dimensional Oxides . . . . .	199
5.5.1	Crystal Structure of $\beta\text{-Na}_x\text{V}_2\text{O}_5$ . . . . .	199
5.5.2	Electronic Properties of Na–Vanadium Bronze . . . . .	200
5.5.3	Magnetic Properties . . . . .	205
5.5.4	Specific Heat . . . . .	206
5.5.5	EPR and NMR in $\text{Na}_x\text{V}_2\text{O}_5$ . . . . .	207
5.5.6	Molybdenum Bronzes . . . . .	209
5.6	$\text{NiO}$ : Origin of the Band Gap and Hole Conduction . . . . .	213
5.6.1	Optical and Magnetic Properties . . . . .	213
5.6.2	Transport Properties . . . . .	216
5.6.3	Electronic Structure . . . . .	221
5.6.4	Electronic Structure of Acceptor Level . . . . .	225
5.6.5	Band Theory of Mott Insulators . . . . .	227
5.7	Perovskite-Type Mn Oxides: Magnetoresistance . . . . .	230
5.7.1	Crystal Structure . . . . .	230
5.7.2	Ferromagnetic Metal–Paramagnetic Insulator Transition . . . . .	231
5.7.3	Electronic Structure . . . . .	234
5.7.4	Charge and Orbital Ordering . . . . .	236
5.7.5	Polaron Effects . . . . .	237
5.8	$\text{Fe}_3\text{O}_4$ , Verwey Transition . . . . .	243
5.8.1	Phase Diagram of the Iron–Oxygen System . . . . .	244
5.8.2	The Spinel Structure . . . . .	246
5.8.3	Verwey’s Model: Order–Disorder Transformation of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ . . . . .	248
5.8.4	Comment by Anderson: Frustration on the $B$ Lattice . . . . .	250
5.8.5	Transport Phenomena and the Fluctuation of Charge . . . . .	252
5.8.6	Band Structure . . . . .	259
5.8.7	Fluctuating Local Lattice Distortion and Electron–Phonon Coupling . . . . .	263
5.8.8	Itinerant Versus Localized Character of Carriers . . . . .	268
5.9	High- $T_c$ Superconductors . . . . .	270
5.9.1	$d\gamma$ Conductors . . . . .	271

5.9.2	$\text{La}_2\text{CuO}_4$ .....	272
5.9.3	$\text{La}_{2-x}\text{M}_x\text{CuO}_4$ .....	276
5.9.4	$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .....	288
5.9.5	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .....	305
<b>References</b> .....		321
<b>Index</b> .....		361